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SEMI-ANNUAL REPORT

OF

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List of abbreviations.

d = specific gravity.

$d_{20^{\circ}}$ = specific gravity at 20° , compared with water at 15° .

$d_{\frac{20^{\circ}}{4^{\circ}}}$ = specific gravity at 20° , compared with water at 4° .

$\alpha_{D20^{\circ}}$ = optical rotation at 20° , in a 100 mm. tube.

$[\alpha]_D$ = specific rotation.

$n_{D20^{\circ}}$ = index of refraction at 20° .

Sol. p. = solidifying point.

M. p. = melting point.

B. p. = boiling point.

n = normal.

Acid no. = acid number; ester no. = ester number; sap. no. = saponification number.

g. = gram; cc. = cubic centimeter; mm. = millimeter.

Temperatures are uniformly given in degrees Centigrade.

The strength of alcohol, if not otherwise indicated, is given in per cent. by volume

Miltitz near Leipzig, April 1, 1909¹⁾.

It is unfortunately impossible to say much that is cheerful about the period reviewed in the pages of the present Report. As we were already compelled to place on record in November last, the year 1908 moved under the sign of economic depression, which in the nature of things made itself especially severely felt in the principal industrial countries, viz., Germany, Great Britain, and the United States. The continual decline in value of raw materials hampered enterprise in all circles where our products are consumed, and the mere fact that in spite of the favourable conditions which prevailed in the money market, important transactions in the staple articles of our trade were entirely wanting, should be sufficient proof that among those concerned confidence in the proximate revival of the general state of trade was still looked for in vain. In any case, those optimists have been proved to be mistaken who prognosticated from the return of sounder economic conditions in the United States an immediate reaction upon our European markets; for in spite of the favourable reports which have been received from America since the beginning of the present year (especially as regards transactions in our branch of industry) it is unfortunately true that as yet there can be no question of any noticeable improvement in business in this particular quarter.

So far, the wounds which have been caused by the financial crisis in all circles where our goods are consumed have only been partly healed, and the consequences of the general falling off in values, which have found expression in serious losses on the stocks remaining over from the record year 1907, are being felt everywhere. It is only within the last few months that the sales have again reached figures denoting a tolerably healthy demand for consumption, and no doubt many more weeks will elapse before it will be possible to report of a genuine revival of interest on the part of consumers.

The decline in the exchange of commodities belonging to our branch of business with foreign countries finds expression in the fact that the imports of essential oils²⁾ into Germany in the year 1908

¹⁾ The commercial part of this Report has been compiled during March.

²⁾ German Official Statistics of Merchandise, No. 353 b and c.

amounted only to 911,300 kilos against 1,498,600 kilos in the year 1907, while the exports fell from 491,700 to 445,300 kilos.

The considerable decline in the imports is traceable to the small demand for those varieties of oils which are imported by Germany from abroad, either for the purpose of manufacturing them into perfumes, or for refining. The further course of business in the current year will depend in the first place upon the question whether it will be possible to remove finally the state of political tension which has been the chief topic of conversation for many months and which threatens to light the torch of war in Eastern Europe. If diplomacy should succeed in suppressing the danger of war and if our friendly relations with the other European Powers (relations which have recently been improved by our understanding with France in the question of Morocco and by the visit of the King of England) should be maintained, the hope for a return of better times will doubtless be fulfilled. In such an eventuality, the only thing to be wished for is that the improvement should not occur too rapidly, as otherwise the danger of renewed reaction would be too great.

Unfortunately the economic condition of Germany continues to be influenced by the unfavourable situation of the Imperial finances and the recurrence of adventurous proposals of financial reform, which are a sequence of this condition. In the interests of our own industry it is especially desirable that a final decision will soon be reached with regard to the Spirit Bill, in order that this much-debated subject may at last be cleared up.

In spite of the generally unfavourable state of business, our Austrian branch in Bodenbach (Bohemia) was comparatively well at work, and it cannot be said that the ancient race-hatred between Bohemians and Germans has exercised a really unfavourable influence upon business in the districts where it prevails, although, especially within the past few months, it has broken out on repeated occasions. The boycotts proclaimed by either side against the other mostly came to nothing, which is a sign that the movement does not affect all classes of the population to an equal degree. The alarming reports about the conflict with Servia, with all the consequences that might follow from it, have of course occupied the principal place in public interest in Austria recently. Although the result of a warlike conflict between the two States could not for a moment be in doubt, such a solution of the dispute might have effects upon the European Peace, the extent of which it would be impossible to foresee. We are still awaiting the new Austrian Spirit Bill already referred to in our last Report, but it has lately been asserted that it may be expected to come into action next autumn.

The commercial and industrial depression in Great Britain, to which we referred in our November Report, has unfortunately not undergone

any marked improvement since then. Business generally has been exceedingly slack and dragging, with comparatively small transactions, and especially as regards the soap industry, very little news of an optimistic character can be reported. On the contrary, in this branch of business competition has become even more keen, with the result that the few large transactions which were carried into effect had to be closed at prices which, in the case of first-quality goods, can hardly pay any of the parties concerned. England continues to suffer perhaps in a larger measure than any industrial country on the Continent from the after-effects of the American crisis, and this fact, taken together with the far-reaching radical, nay, almost socialistic legislation of the last few years, which can hardly be justified financially, no doubt paralyses all trade and traffic, with the result that a healthy development of business enterprise appears to be downright unattainable.

A comparison of British over-sea-trade in the year 1908 with the foreign trade of the competing Nations (among which, we may remark in parenthesis, Germany appears to have lost the least ground) may here be of interest. The decline in exports was as follows¹⁾: —

From the United Kingdom . . .	11,4 %
„ „ United States . . .	8,7 %
From France	5,8 %
„ Belgium	4,3 %
„ Germany	1,4 %

Australia continues to occupy the principal position of interest among the British Colonies. According to the Report of the Hamburg Chamber of Commerce, the decline in the price of wool has caused a serious want of available capital in that country, and even at the present time the scarcity of money has not been quite overcome. German exports to Australia have, moreover, been injuriously affected by the preferential duties in favour of the Mother Country established under the Australian Customs Tariff, which was provisionally applied last year, and which has since come into action. The sale of German goods is further unfavourably affected by the absence of goodwill (we quote from the above-mentioned Report) which is often shown in Australia towards German trade and German merchandise. So far as our own experience goes, we are unable to give an unqualified endorsement to this view, for even under the new Customs Tariff the sale of our manufactures so far has continued to develop in an entirely satisfactory manner.

The final settlement of the Morocco question, which has so frequently threatened to destroy our friendly relations with France, has been received everywhere with lively satisfaction. Particularly in our

¹⁾ Compare Report November 1908, 5.

industry, which has gradually created for itself a leading market in the important neighbouring country of France, every step is welcome which brings the two nations closer together economically. Of course the future alone can show in how far the peaceful settlement of this question will influence the general relations between Germany and France. In any case it is to be regretted that simultaneously with this settlement another problem has appeared, which must unfortunately be regarded as seriously endangering the commercial relations between France and Germany after having been built up with so much trouble. We refer to the new French Customs Tariff, in which it is proposed materially to increase the Customs duties upon almost all articles in our branch of business. Great Britain has already protested sharply against the proposals of the French Customs Commission which are obnoxious to trade, and we trust that in case no means should be available of taking action against the proposals by diplomatic proceedings, the *Comité Commercial Franco-Allemand* in Paris will at any rate do its utmost to prevent the French Protectionists from being victorious. It can certainly not be maintained that under the protection of her Customs Tariff France has undergone a particularly remarkable industrial development, for it can be proved without doubt that so far as capacity of output is concerned, French industry is very far behind that of Germany and England. The trade between France and Germany has of course suffered during the past year as a result of the general depression. According to the *Documents statistiques sur le Commerce de France*, it reached the following figures (in 1000 fr.): —

1908		1907	
Imports	Exports	Imports	Exports
626 340	640 876	638 157	649 693

Referring to the new French Pharmacopœia discussed in our last Report, we may here mention that by Decree of the French Government dated 17th October 1908, a period of transition of 8 months — that is to say up to May 15th 1909 — has been fixed, at the end of which all medicinal preparations used in France must comply with the new conditions.

In Spain, the condition of affairs in those branches of business in which our articles are employed, continues to be by no means satisfactory, notwithstanding that the proposals for the spirit tax reform have in the meantime come into force. The Spirit Bill which was enacted many years ago by Osmá and the provisions of which have had far-reaching consequences, has at last been replaced, on the 10th December 1908, by a new Act. This measure possesses certain improvements upon its predecessor, but most of the old disadvantages have been retained, and several important new ones have

been added. The advantages of the Act are the conversion of the varying duties which formerly prevailed, into a uniform duty, which has been reduced to 20 pesetas for spirits of wine, and 50 pesetas for industrial alcohol per 100 liters of 90 to 95°, the previous duties having averaged about 60 and 110 pesetas respectively. On the other hand, however, the Act has created untenable conditions, and has caused great confusion, by prohibiting pharmacists, druggists, etc., from purchasing or retailing essences and oils which are used in the manufacture of brandy and liqueurs, and compelling the distillers to buy such articles directly from the manufacturers. As a result of protests, concessions were made to pharmacists, perfumers and confectioners, and as it seems hardly likely that druggists can be permanently kept from sharing in these concessions, it follows that the prohibition above referred to has in point of fact become a dead letter even at the present time. But the complications and delays remain in existence to their fullest extent, and these are increased by the fact that often the Authorities themselves do not know how to interpret the letter of the Act. Through our General Agency in Madrid we immediately took the necessary steps to be able to do justice to the requirements of the trade in our articles in Spain under the new conditions prevailing, and we hope soon to be able to report a satisfactory improvement in business.

The provisions of the new German Commercial Treaty with Portugal have not yet been published, but in the meantime the unanimous opinion with regard to it is one of disapprobation. It would really be incomprehensible if German diplomacy should surprise the Nation with a treaty, the advantages of which, as is said to be the case, are entirely on the side of the other party.

Our Eastern neighbour Russia has further recovered from the wounds of the war and the now suppressed revolution. The gallows, however, continues to do its work there, and the prisons are overcrowded; but if the Duma should succeed in acquiring the confidence of the country, the economic revival of this mighty Empire may perhaps be assured. Unfortunately, the political situation in Russia is very closely connected with the Balkan question, and it will depend upon the solution of the Servian conflict whether the blessings of peace abroad and at home — which have been attained at such heavy sacrifices — will or will not continue to be enjoyed.

With regard to the Scandinavian countries, all that has to be reported is that preliminary steps have been taken in Sweden for subjecting the Customs Tariff to revision before negotiations are commenced for the renewal of the Commercial Treaty with Germany of 1905, which expires next year. Unfortunately, this revision is not likely to be carried out without a number of increases in Customs

duties; but it is to be hoped, for the sake of Swedish industry, that the products of our industry, seeing that they count among the raw materials, shall at any rate not be made subject to higher duties than are now prevailing.

Nothing special can be reported with regard to our intercourse with the Balkan States, and it will be desirable to suspend all expressions of opinion as regards the future of this market until the Servian question has been finally solved. In Turkey, the introduction of a Constitutional régime is still too much in the state of transition to make it possible, at this early period, to point to any beneficial results from this measure of civilisation, or to the recovery in a material sense of the Nation under the sway of the now ruling Young Turkish Party.

The other consuming countries in Europe offer no occasion for special comment; but we cannot conclude this part of our review without a reference to the tragic occurrences in the Far South, the news of which horrified the world at Christmas time. Messina and Reggio, two flourishing cities, have fallen victims to the catastrophe of an earthquake, the like of which is not recorded in the history of the world, and without any presentiment of disaster, thousands of the inhabitants have met their death under the ruins. The entire civilised world deplores with Italy the loss of so many lives, and extends its sympathy in their misfortune to the few remaining survivors, nearly all of whom have lost home and chattels. All our readers know the important position occupied by the two severely tried cities in the trade in Sicilian and Calabrian essential oils, and all will understand that the catastrophe has necessarily resulted in changes in the commerce of these products, the effect of which we are as yet quite incapable of surveying. To our great delight we are able to report that our esteemed friend, Mr. Eduardo Jacob, who has also been our valued collaborator in these Reports during several decades, has been fortunate enough, together with his family, to escape a tragic fate; and we are glad to take this opportunity of again sincerely congratulating him upon his wonderful escape. Mr. Jacob has supplied us with a report which at last enables us to give an authentic account of the condition of things in the regions affected by the earthquake, and in view of the difficult conditions under which his report was composed, we owe him our especial gratitude.

The hope which we expressed in our last Report that in accordance with the experience in previous Presidential Elections, business in the United States would revive immediately after the close of the Electoral campaign, has not been fulfilled in its entirety. During the closing months of the year also there was no real recovery in business-transactions, although a marked feeling of confidence had taken

session of all commercial and industrial circles since it had become known that the Republican party would remain at the helm, — that to say, that the contest between Taft and Bryan had been decided in accordance with the wishes of the Eastern States, whose interests are principally connected with foreign trade. Our New York Branch informs us that during the first two months of the New Year business has been extraordinarily animated, and from this fact it draws the satisfactory deduction that trade and traffic are positively, although slowly beginning to revive. Unfortunately, a new spectre has arisen in the form of the impending revision of the Customs Tariff, which is to be carried out as a matter of urgency by the new President. This event is not looked upon without apprehension in all industrial circles in Germany, as it threatens to block the revival of commercial relations with the United States. For the present nothing can be said as to the extent to which various classes of industrial products will be affected by changes, and the answer to the question whether or not the revised Tariff contemplates increases in the Customs duties upon our essential oils and perfumes, must still be left to the future.¹⁾

It is a matter of especial satisfaction that a Treaty has recently been entered into between the United States and Germany, in which both countries grant each other complete freedom in the matter of the exploitation of patents, and by virtue of which inventors as well as owners of patents will enjoy equal treatment in both countries. The text of the agreement will only be published when the Treaty has been ratified by the Senate. In any case, this result of mutual good-will will be warmly applauded, especially in view of the injury done to German inventors and patentees by the compulsion to work their inventions in the country itself, such as in Great Britain.

The statistics published after the close of the year 1908 proved that, both as regards foreign trade and industrial production in the

¹⁾ Our New York branch mailed on March 31st the following supplementary information: —

“According to the official text of the Payne Tariff Bill, a number of important Essential Oils have been omitted from the Free List, which would bring them under the general head of «Unenumerated Essential Oils» at 25 % ad valorem.

“The striking feature in the selection of these oils, none of which are manufactured in the United States commercially, finds ready explanation in the strong desire of the originator of the Bill to provide revenue.

“However, there is an almost endless discussion pro and con (already well started) to be looked for, and whatever the end may develop, its intermediate waste of time, and concomittant uncertainties, will seriously disturb not alone the market of the United States, but also of the whole World.

“It is doubtless of great importance for the manufacturing interests of the United States to retain certain Essential Oils on the Free List, but we deem it, under the present tentative condition of the Payne Bill, futile to point out, beyond the above general reference, certain other inconsistencies affecting our line.”

United States, 1908 must be regarded as a year of retrogression compared with 1907, although the last quarter of 1907 also suffered from economic depression. The total imports of the United States in 1908 were of a value of \$ 1.116.000.000 against \$ 1.423.000.000 in 1907, showing a decline of \$ 307.000.000, or 21 ½%. The total exports from the United States in 1908 were \$ 1.753.000.000 against \$ 1.923.000.000 in 1907, so that the falling off on the year amounted to \$ 170.000.000, or 8,8 ½%. It is chiefly owing to the heavy exports of copper, showing a surplus of 295.000 tons, that the decline in exports has been limited to 8,8 ½%. The imports of New York, which consist chiefly of manufactured goods either for consumption or for use in industrial processes, has fallen by \$ 188.000.000, or 25 ½%, and the receipts of the Customs in New York were \$ 3.600.000, or 17 ½% below those of 1907.

These data, which we take from the report of the Commercial Expert at the German Imperial Consulate-General in New York, are too clear to need comment, and show the past business year to have been an entirely unsatisfactory one for the United States.

Although in the Argentine the decline in the price of wool, an article of enormous importance for that country, has disturbed industrial progress, the excellent harvest, the produce of which has found a ready sale, has more than recompensed for the loss on wool. The heavy stocks of imported goods, which at first threatened to bring disaster, were soon cleared, and a healthy business demand was developed, in which our industry has also taken its share.

In Uruguay similar conditions prevailed, except that in the first half of the year the unfavourable state of the wool market was still more heavily felt there. The merchants in the interior of the country passed through serious times, and the slowness with which money was paid in, as well as a general disinclination for business, reacted upon the import houses in Montevideo. Recently confidence in the future has been regained, as the harvest prospects are good, and the purchasing power of the population of the back-country may consequently be considerably increased.

As a matter of course, the general crisis has not passed over Brazil without leaving an impression, and the sales of goods in the interior of the country were occasionally seriously impeded. In the Northern part of the Republic business was especially affected by the fall in the price of india-rubber, and in Central Brazil by the increased export duty on coffee. But as towards the end of the year the rubber market improved again and as the further extension of coffee plantations is being put a stop to by the introduction of rice cultivation, there is every appearance that better times are in store.

In the Official *Jornal do Commercio* of January 30th 1909, the summaries relating to the foreign trade of Brazil in the past 3 years,



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which had appeared in previous issues, are of official statistics dealing with the month in the value of the exports in December.

December 1907 was about £ 1,400,000, or 39%. On the other hand, in December 1908 there has again been a heavy decline in the imports amounting, in round figures, to £ 1,100,000, or over 40%. The total results are as follows: —

	1906 £	1907 £	1908 £
Value of Exports	53 059 470	54 176 898	44 094 992
Value of Imports	33 204 041	40 527 603	35 491 410
Active Commercial balance in the exchange of commodities	19 855 429	13 649 295	8 603 582

The state of trade in Chile during the past year has given small cause for satisfaction, owing to the events of the two preceding years, such as earthquakes, excess of speculation, and the general commercial crisis. The rate of Exchange fell to a point which had never before been reached (about $7\frac{3}{4}$ d.), from which it only recovered towards the end of the year up to about $12\frac{3}{4}$ d. The over-supply of the market with all kinds of import articles — among others particularly by the consumers of the products in which we are interested — brought about an extremely sluggish condition of business, yielding very little profit and occasionally being altogether at a standstill. It is true that in the course of the past year three factors — viz., a good harvest, which realised satisfactory prices on account of the depreciation of the currency; secondly, an increased output of copper, notwithstanding the lower prices; and thirdly, a considerably diminished importation, contributed to counteract a further worsening of the general state of trade; but unfortunately a decided and lasting improvement still appears to be far distant. In the neighbourhood of Valparaiso and Santiago the crop this year has been a failure on account of drought, and in the Northern part of the country many of the nitrate works are suffering from over-capitalisation or mistakes in management, although the prices of nitrate of soda have not been unsatisfactory. It is probable that only the renewal of the Nitrate of Soda Trust (if this should come about) would again bring some improvements in the prospects of the financially weak companies, which otherwise will have to stop working in face of the competition of the better-situated older concerns. Another cause why careful business people are adopting a waiting policy with regard to Chile lies in the danger, which is still threatening, that in spite of the bad economic condition and notwithstanding its many opponents, the Act on the re-introduction on 1st January 1910 of the Gold Standard (18 d.), is strictly carried out. It is evident that the autocratic, untimely, and entirely doctrinal enforcement of this Act (which no doubt was decreed with the best

motives) would be attended with the most serious consequences in the thoroughly altered conditions which prevail. This has been sufficiently shown by the example of the Convention of 1895, which was also artificially arranged and which ultimately collapsed in 1898, after 3 years of stress. Under such economic conditions the re-building of the city of Valparaiso on a modern plan is only being slowly completed. Moreover, the many opponents of the scheme for the construction of a new harbour have succeeded in causing this project — which is of such extreme importance — again to be deferred for an indefinite period. As a result of the enormous decline in the imports and thanks to the united efforts of the shipowners and Insurance Companies, it has been possible again to restore the necessary order and despatch in the loading and discharging of ships and in the Custom House work along the entire coast; and it is therefore probable that the complaints which have been made on this score for so many years may soon cease altogether. After the settlement of its differences with Peru in the matter of the delimitation of the boundary line, the satisfactory solution of the question of the currency, and the brightening of the prospects of the nitrate industry, a time of vigorous economic revival may again dawn for Chile, notwithstanding the prognostications of the pessimists, who less than a year ago indulged in the darkest prophecies.

On the subject of the soap business in Cuba, an American Consular Report contains a short article which possibly may induce our friends in the toilet soap branch to give increased attention to Cuba as an export market. It is stated that practically all the soap which is used in Cuba is imported, local manufacture being chiefly restricted to the preparation of highly scented toilet soaps. The annual imports of common soap in bars amount to about 9000000 lbs., of which about 12% come from the United States, 80% from Spain; and the rest mostly from France. Of toilet soap, about 150000 lbs., in round figures, are imported; of this 50% come from the United States and 45% from France. The imports of all other soap together amount to approximately 325000 lbs., of which 75% are from the United States and 20% from France.

With regard to the economic condition of Japan and the prospects of German trade in this interesting market, opinions vary profoundly; but it is an undeniable fact that the financial condition of the people of Japan has been seriously injured by enormous increase in taxation during the last few years, and that the purchasing power has been greatly diminished among all classes. The country will also continue to suffer for a long time from the results of the unscrupulous exploitations on the part of industrial speculators, to which we have already referred on previous occasions. The prevailing low prices in all its

Principal articles of export, such as copper, silk, camphor, etc., have greatly diminished the profits of the export trade. In addition to this, the exports to China — which country forms the principal outlet for Japanese industry — continue to be halting and even threaten to degenerate into an entire boycott of Japanese products. All these facts contribute to make the condition of trade look by no means rosy; but on the other hand, less pessimistic reports are not wanting, and these indicate a gradual, albeit slow, improvement of the economic conditions. It is, for example, regarded as a favourable factor that the rice crop of 1908 has been an extremely good one, as a result of which the import of rice (the staple food of the Japanese) from Burmah and Tonquin has considerably decreased. In forming an opinion of the import figures, which we quote below, this not unimportant item must be allowed for. Our own experience of the last few months makes it impossible for us to deny that there has been a perceptible improvement in business, which we trust will continue. In one of the recent issues of the *Ostasiatischer Lloyd*, we find a few interesting figures relating to the Foreign trade of Japan. According to this, the total value of Japanese trade with foreign countries was as follows: —

Year	Exports	Imports	Total of foreign trade
1903	311212000 yen	332119000 yen	643351000 yen
1904	341112000 „	384586000 „	825678000 „
1905	344368000 „	500001000 „	844369000 „
1906	423754000 „	418784000 „	842588000 „
1907	430516000 „	494192000 „	924708000 „
1908	373796000 „	435687000 „	812483000 „

In the course of the past year both exports and imports have declined considerably, but whereas the exports have almost gone back to the figure of the year 1905, the imports (not counting the year 1905, when Japan was at war with Russia) were the highest, with the exception of the year 1907.

As an appendix we bring an interesting paper “On the examination of the Essential oil of *Blumea balsamifera* D. C.”, by Mr. Richard Jonas, of Brussels. This examination has been partly carried out in our Laboratory.

We also call especial attention to the “Solubility Table of the most frequently used Odoriferous Substances”, which, at the instance of some of our clients, we have caused to be prepared (page 142).

Commercial notes and scientific information on Essential Oils.

Almond Oil, bitter. We refer below to the position of the market in this article.

Almond Oil, pressed from almonds, Ph. G. IV. Our sales of this specialty still continue to increase, and at times the demand has been so great that our output was unable to keep pace with it. Generally speaking, the prices of almonds have undergone no change, for fortunately the rumour that about 8,000 bales of almonds had been destroyed in the catastrophe at Messina proved to be exaggerated, and the advance in prices which resulted thereby was consequently only a passing one. The producing districts in Sicily, which are in the neighbourhood of Girgenti, have fortunately remained unaffected by the earthquake. Efforts have recently been made in Apulia, to increase the demand for the article, and reports have been spread, with this end in view, that there has never been any instance of three good harvests in succession. Moreover, it is said that owing to the drought which prevailed last year the plantations have seriously suffered in parts.

Almond Oil, pressed from apricot kernels. Since apricot kernels have become an article of speculation, it grows more and more difficult to give a commercial report on this commodity. The fear expressed in our last Report that a fresh effort would be made to drive up the prices to the high level which they reached in the course of the summer has fortunately not been realised, for which no doubt the general lack of enterprise is the chief reason. It is to be noted that not only in Damascus, but also in all other districts where apricot kernels are produced, the stocks were very much reduced towards the end of the year, and even in California, where a bumper crop was talked of as early as the spring of 1908, nearly all the supplies have gone into consumption. The stocks in the hands of middlemen in Hamburg, Marseilles, Genoa and Trieste were also practically cleared at the close of the year, with the result that prices rose to about 78 marks per 100 kilos. If a more lively demand should now ensue, — a contingency which, however, is hardly to be expected in view of the general state of business — it is not impossible that the speculators may gain the upper hand and that we may be face to face with a scarcity similar to that which prevailed a year ago. At the present time it is still impossible to form an opinion as to the result of the current year's crop in the principal growing districts, Syria and California; and it is therefore quite out of the question to

we even a guess at the further course of the market. In any case the quotations of our almond oil pressed from apricot kernels, which as a result of large stocks we have been able to reduce slightly, are scarcely likely to undergo a further reduction within the near future. The prices of essential oil of bitter almonds have remained unchanged, and the fact that we are never able to accumulate any stock of this article is sufficient proof that we are gradually succeeding in maintaining our position in competition with cheap and adulterated qualities.

With regard to the theories on the course of the decomposition of amygdalin by emulsin, represented by Feist and Rosenthaler respectively and referred to in our last Report¹⁾, further communications have been published by both authors.

K. Feist²⁾ is unable to see in Rosenthaler's experiments a disproof of his view that in the course of the splitting-up, primarily d-benzaldehyde cyanohydrin is formed. He regards the action of the emulsion as a reversible catalytic process: d-benzaldehyde cyanohydrin + emulsin $\rightleftharpoons$ benzaldehyde + prussic acid + emulsin.

L. Rosenthaler³⁾ asserts that he merely regards Feist's proofs as insufficient, leaving the question of the accuracy of Feist's theory an open one. In another detailed treatise on asymmetric syntheses effected by enzymes⁴⁾ he reports more fully on his researches, of the results of which the following is a synopsis: —

The synthesis of d-benzaldehyde cyanohydrin from benzaldehyde and prussic acid by the action of emulsin is effected by a constituent (s-emulsin) which differs from that upon whose action the hydrolysing property of emulsin is based (d-emulsin). This s-emulsin possesses enzymatic characteristics and as regards its action an optimum could be found according to time and temperature. Apparently the s-emulsin is either used up in the synthesis, or it passes into an inactive phase. During the experiment it was not decomposed by chloroform or benzaldehyde, although the last-named combination showed noxious effects. In any case, the reaction (the course of which was influenced by varying quantities of the reagents and by variations in the execution of the experiments), proceeds as follows. In the first place the prussic acid enters into a loose combination with the optically active constituent of the emulsin; next the benzaldehyde attaches itself to the residual prussic acid of the compound, forming an asymmetric carbon atom;

¹⁾ Report November 1908, 14.

²⁾ Arch. der Pharm. 246 (1908), 509.

³⁾ Ibidem 710.

⁴⁾ Biochemische Zeitschr. 14 (1908), 238. Quoted from a copy kindly sent to us.

and lastly the separation takes place of the d-benzaldehyde cyanohydrin from the optically active complex. The mandelic acid which was produced by the saponification of the nitrile was shown by its constants (m. p. 133 to 134°; $[\alpha]_D - 153,78^\circ$) to be polarimetrically pure. Optically active nitriles could also be obtained from anisic aldehyde and cinnamic aldehyde. Enzymes which, in addition to a catalytic action (such as was also found to exist in the case under review), possess a "directing" action, such as had not been observed hitherto, are called by Rosenthaler "asymmetrases". The author is of opinion that such cases as that described by him afford data for an understanding of the process of asymmetric syntheses in plant-cells.

With regard to a method for the colorimetric determination of benzaldehyde in extracts of bitter almonds, see Analytical Notes.

Aloe wood Oils. Moszkowski¹⁾ has published a few short notes on the subject of the Javanese scented wood *Kaju garu* (*Kaju gaharu* = eagle wood) which we described in our last Report²⁾. He has found in Sumatra the tree which yields the "eagle wood", and which is locally known as *Karas*, and describes it as a fine tree, often reaching a height of 40 meters, with a smooth, grey bark and a splendid umbrageous crown. In general, his statements with regard to the wood and the method by which it is obtained agree with those of Boorsma³⁾. On the other hand, Gilg, who examined a branch without blossoms or fruit gathered by Moszkowski, classifies the plant botanically as a new species of *aquilaria* (*Aquilaria Moszkowskii*) which is stated to be most nearly allied to *Aquilaria malaccensis* Lam. and *Aquilaria grandiflora* (Lour.) Gilg, whereas according to Boorsma the *Kaju garu* of Java is derived from *Gonystylus Miquelianus* T. et B.

Andropogon Oils. As a result of a communication in the last Buitenzorg Annual Report⁴⁾, we are able to amplify a note in our last Report on the subject of the oil of an unknown variety of *Andropogon* which had been examined at the Buitenzorg Botanical Institute⁵⁾, by stating that the oil in question contained geraniol to the extent of 18,7% esterified, and 30,1% free, geraniol.

Furthermore, an oil of *Andropogon intermedius* has been examined in the said Institute⁶⁾. This oil had a specific gravity of 0,889 (26°) and an optical rotation $\alpha_D - 21^\circ 52'$.

¹⁾ Notizblatt des kgl. botan. Gartens und Museums zu Berlin-Dahlem, No. 43 (Vol. V.), 8 and 83.

²⁾ Report November 1908, 19.

³⁾ Ibidem.

⁴⁾ Report November 1908, 72.

⁵⁾ Jaarboek van het Departement van Landbouw in Nederlandsch-Indië 1907, 67. Batavia 1908.

⁶⁾ Ibidem.

From a new, likewise unknown *Andropogon* variety¹⁾ an oil was obtained at Buitenzorg with a lævorotatory power of $4^{\circ} 8'$, lack of material preventing the determination of further constants.

Possibly the last-named oil may have originated from the same plant of which Dr. de Jong, of Buitenzorg, kindly sent us a small sample of oil, with the observation that it had been obtained from a yet unknown variety of *Andropogon*. In order to distinguish this one from that previously referred to²⁾ we will designate it as "*Andropogon* variety no. 2". This oil was pale yellow and had a peculiar odour, reminding at the same time of fatty aldehydes and of geraniol or methylheptenone; $d_{15^{\circ}} 0,9961$; $a_D - 2^{\circ}$; $n_{D20^{\circ}} 1,51236$; acid no. 3,6; ester no. 7,3; soluble in 1 vol. of 80 per cent. alcohol; when 3 vols. are added the sample becomes cloudy. The oil reacted with bisulphite of sodium, and the product of reaction, when decomposed with carbonate of soda solution, yielded a fatty aldehyde which is possibly identical with decylic aldehyde, but which could not be examined in detail on account of the insufficiency of the material available.

Angelica Oils. In October last, as we reported at the time, the moment when the newly-distilled oil would be available was looked for with much impatience, and everywhere high prices had to be paid. Naturally, growers in Thuringia took advantage of the favourable position of the market for angelica root, and as a result of the strong competition it was difficult to obtain supplies. Our own cultivations have yielded an excellent material, and have enabled us to complete our supplies with a distillate of exquisite quality. The prices of pure angelica root oil ranged at first from 90 to 95 marks per kilo, but gradually advanced to 140 marks, and are still threatening to increase further. This movement of prices indicates that in all probability we are approaching a similar, if not still more severe, scarcity as that which prevailed last year, and that this season, too, far less oil will be produced than is required. Angelica seed was so dear that we did not feel inclined to risk distilling it, and for this reason we are not quoting angelica seed oil in our price list. Fortunately the demand for this article was so insignificant that its absence was not followed by any inconvenience.

Anise Oil. The comparatively low prices of the previous autumn, which enabled us again to take up the distillation of Russian aniseed, unfortunately did not last long, and we were therefore unable to secure even an approximately sufficient supply for our requirements. The aniseed market gradually advanced by 6 to 7 marks per 100 kilos, because a strong demand for export, especially to France, was ex-

¹⁾ Ibidem.

²⁾ Report November 1908, 72.

perienced in Russia. The consumption of Russian oil of anise has of course decreased very considerably since anethol, which was first brought into commerce by us, has not only established itself in the manufacture of liqueurs, but has also been introduced in almost all modern Pharmacopœias.

Oil of *Artemisia lavandulæfolia*. The oil of *Artemisia lavandulæfolia*, a plant growing wild in the Tengger Mountains (Java), has been examined by the Botanical Institute at Buitenzorg.¹⁾ It had $d_{26^{\circ}} 0,924$ and rotation $\alpha_D -7^{\circ} 32'$. On cooling, the bulk of it solidified and the crystals which separated out in the congealing process appear to possess the molecular formula $C_{12}H_{14}O_2$, but owing to the lack of sufficient experimental material it was impossible to determine the structure of the compound.

Basil Oil. From the South of France we received two light brown distillates, from the species known there as *Basilic nain* or *petit basilic* (*Ocimum minimum* L.) which agree as to their constants with the current commercial oils of German and French basil from *Grand basilic* (*Ocimum basilicum* L.), while differing markedly from the latter in their peculiar aromatic odour and their chemical composition. The two distillates in question contain about 14 % of eugenol, which was identified by its benzoyl compound (m. p. 69°). Linalool also appears to be present, at least the phenol-free portions of the oil had a distinct linalool odour. Whether the specimens also contain methylchavicol, the principal constituent of the oils of commerce, we were unable to determine, because the samples at our disposal were too small. For this reason, too, our examination was necessarily almost limited to the ascertainment of the general constants: —

	$d_{15^{\circ}}$	α_D	Acid no.	Ester no.	Phenol cont.	Solubility in	
						80 p. c. alc.	70 p. c. alc.
1.	0,9102	$-11^{\circ} 58'$	5,3	12,5	14 %	in 0,6 vol. and more	in 2 vol. with 10 vol. opal.
2.	0,8901	$-13^{\circ} 36'$				in 1 vol. and more	in 2,5 vol., from 4,5 vol. upwards cloudiness.

Bay Oil. The sale of this article is becoming slower and slower, but as within the past few years the output in the West Indies of cheap bay oil, mostly of doubtful quality, has decreased to a large extent, there is no prospect of any over-production, and prices can be maintained at their present level. It is a pity that so very little interest is shown nowadays for that refreshing article, Bay rum.

¹⁾ Jaarboek van het Departement van Landbouw in Nederlandsch-Indië 1907, 66. Batavia 1908.

Fr. Watts and H. A. Tempany¹⁾, of Antigua, have made researches into the question in how far the age of bay leaves affects its yield of oil and the properties of the oil produced. With this end in view they distilled both young and old bay leaves from Montserrat. The values which were ascertained were of such a character that it is impossible to draw any direct inferences from them.

	Oil yield	Sp. gr. of the oil	Phenol content
Young bay leaves . . .	1,27 %	d _{15°} 0,9648, d _{15°} ^{30°} 0,9507	60 %
Old bay leaves . . .	1,50 %	„ 0,9612, „ 0,9480	61 %
Young bay leaves . . .	1,12 %	— d _{16,6°} ^{28°} 0,9308	53 %
Old bay leaves . . .	1,10 %	— „ 0,9505	60,5 %

It is also worthy of note that, contrary to previous statements in the *West Indian Bulletin*, according to which *Pimenta acris* was said not to flourish in the limestone soil of Antigua, Watts and Tempany report that a considerable number of these trees are found in the island.

Lemon-scented Bay Oil. Whereas the genuine bay leaves are derived from *Pimenta acris* Wight, Watts and Tempany²⁾ state that a variety known as *Pimenta acris* var. *citrifolia* occurs in the West Indian islands which externally resembles the genuine bay tree, but which yields an oil known as "lemon-scented bay oil" on account of the fact that its odour reminds at the same time of bay and of lemon. Both these varieties of *Pimenta* are found growing side by side in the Islands of Dominica, Montserrat, Barbuda, and Antigua. Fishlock has made other investigations with regard to the distribution of the trees in the Virgin Island of St. John, where the genuine bay tree predominates, whereas in Tortola almost exclusively the *citrifolia* variety grows.

Up to the present little is known concerning lemon-scented bay oil. An oil of this kind distilled many years ago by J. H. Hart possessed, according to our determinations, a specific gravity of 0,882 (25°) and an optical rotation of — 0° 37'. The presence of citral was shown by the preparation of α -citryl- β -naphthocinchonic acid³⁾. The citral content afterwards determined by Watts and Tempany by the bisulphite process was 65 %/o. The last-named authors have lately prepared a similar oil themselves from leaves grown in the island of Tortola. They obtained a yield of 1,11 %/o of a pale yellow oil of a pronounced lemon-like odour with a peculiar additional aroma reminding

¹⁾ West Indian Bulletin 9 (1908), 273. From a copy kindly sent to us.

²⁾ West Indian Bulletin 9 (1908), 275. From a copy kindly sent to us.

³⁾ Report October 1896, 73.

of cress: $d_{16,60}^{270}$ 0,8937, α_D — 0,16°, citral content 44 %, phenol content 10 %; the oil dissolved completely even in 60 per cent. alcohol. Unfortunately the volumetric proportion of solubility is not stated.

Calamus Oil, Javanese. A calamus oil distilled by Dr. Carthaus in Java has been examined at the Botanical Institute in Buitenzorg¹⁾ It possessed the following constants: $d_{260}^{1,06}$, $\alpha_D + 0^\circ 52'$, sap. no. 9.

We have had an opportunity of examining two calamus oils from the same source which behaved very similarly. They had a yellow colour and a faint calamus odour. The constants of the one were: $d_{150}^{1,0783}$, $\alpha_D + 0^\circ 53'$, $n_{D200}^{1,55043}$, ester no. 12; of the other: $d_{150}^{1,0771}$, $\alpha_D + 0^\circ 51'$, $n_{D200}^{1,55065}$. The oils here referred to differ from ordinary calamus oil in their greater specific gravity, their much lower rotation, and their higher index of refraction. In normal calamus oil these values range within the following limits: $d_{150}^{0,96}$ to 0,97, $\alpha_D + 9$ to $+ 31^\circ$, n_{D200} about 1,506. Moreover, the Javanese oils are already soluble (with slight separation of paraffin) in 1 to 1,5 vol. of 70 per cent. alcohol, while ordinary calamus oil is only soluble in 90 per cent. alcohol (in almost every proportion).

Camphor Oil. There has been very little change in the tendency of the camphor oil market during the course of the past five months. The dull state of business, as well as the fact that the existence of important supplies tied the hands of those interested, caused a further reduction in the quotations, and even at the present moment holders in Japan are inclined to accept reduced offers. The shipments from Japan were quite insignificant, except as regards a few thousand cases which were exported to the United States. Within the past few weeks camphor has shown a somewhat more animated tendency, which is probably accounted for by the fact that, since prices have reached a lower level than has been known for a very long time, the competition of artificial camphor may be regarded as entirely removed. For the present we regard it as very little probable that this firmer tendency will also influence the camphor oil market, especially in view of the enormous quantities which must have accumulated in Japan.

Wit regard to camphor plantations in Ceylon, the American Vice-Consul W. C. Doyle²⁾ reports that in 1907 the area under cultivation was increased from 142 to 1106 acres, and that for 1908 apparently a still greater increase was projected. As a result of these extensions a

¹⁾ Jaarboek van het Departement van Landbouw in Nederlandsch-Indië 1907, 67. Batavia 1908.

²⁾ Oil, Paint and Drug Reporter 74 (1908), No. 23, page 52.

perceptible contribution to the World's requirements in camphor was to be expected. The camphor tree does not flourish in the coast region, but it does well in the mountainous districts of the Island, at altitudes between 2 500 and 8 000 feet. The yield of camphor from a cultivated area of from 15 to 20 000 acres is estimated at 8 000 000 lbs., which according to most authorities is the quantity needed to supply the World's requirements, and hopes are entertained in Ceylon that, within the course of a few years, more camphor will be produced in the Island than is consumed on the entire globe at the present time. Among planters, the rapid growth of the branches of the camphor trees is regarded as the cause of the pre-eminence of Ceylon over other camphor-producing countries. The cost of producing natural camphor in Ceylon is estimated to be considerably lower, weight for weight, than the cost of the American synthetic product from oil of turpentine. The first experiments of cultivation in Ceylon were made by the Government with Japanese camphor seed, and the mode of cultivation consists in allowing the tree to reach a height of 40 ft. (which it does in about $3\frac{1}{2}$ years), when it is cut down to 4 or 5 ft. With this object in view the trees are pruned every 4 and sometimes every 3 months. The trees are planted at distances of 4×8 ft., which gives 1360 trees to the acre. Experiments of distillation made with the wood cut from an acre of ground, produced 190 lbs. of camphor. One planter maintains that he has obtained a particularly high yield of camphor by pressing the branches instead of distilling them. But although he vouched for the truth of this statement, he refused to disclose any particulars as to the process.

The Official Customs Statistics indicate that in 1907 a parcel of camphor weighing 562 lbs. was exported from Ceylon, and it is inferred from this that the quantities to be exported annually in the future will increase in geometrical proportion.

An American expert, Prof. Hilgard¹⁾, has written on the subject of the question of the cultivation of camphor trees in the United States, his paper being a sequel to that of Rivière which was discussed by us at the time²⁾ and which takes the same view. Prof. Hilgard has made enquiries from the experts in the Agricultural Department at Washington and in the Southern States of the U.S., as to the prospects of camphor cultivation. The first-named Authorities informed him that although the Government had made experiments in the growing of camphor trees in its Southern Experimental Stations, it doubted greatly in the financial success of such an undertaking, and for this reason it

¹⁾ Journ. d'Agriculture tropicale 8 (1908), 360.

²⁾ Report November 1908, 36.

does not supply camphor seed to any private people, who are able to obtain their requirements of such seed from the trees which had already previously been planted in Florida and California. In most of the plantations the trees are regarded only as ornamental, and are treated as such, but in some of them experiments have been made to obtain camphor by distilling the leaves, either with or without stalks. The results of these experiments are not reported by the author, who only deals with his own experiments in making industrial use of the Californian camphor tree. According to these experiments, mature green leaves yield about 1 per cent. by weight of camphor, and it is to be noted that leaves and green twigs contain more liquid oil and less solid camphor. Up to the present no higher yields of camphor have been obtained. Hilgard observes that he has experimented only with trees growing in the misty, cool climate of the coast, and not with trees from the warmer and higher altitudes, for instance those from the interior of California. Although the latter trees no doubt might promise a higher output, seeing that odoriferous plants such as jasmine, mignonette, and heliotrope also flourish in the interior of California, Hilgard refrained from making any far-going experiments, because of the excessively high wages (for the harvesting of the leaves), which in those districts are an obstacle in the way of the development of the camphor industry as well as of other industries. The author therefore agrees with Rivière that there is no question of any American industrial competition with the natural riches and low wages of the island of Formosa, particularly as just at the present time the prices for crude camphor are low and are likely to remain so.

With regard to the prospects of synthetic camphor, Hilgard is of opinion that any serious competition with the natural product is out of the question until there has been a considerable increase in the present moderate yield, which equals only 25% of the turpentine oil used. Moreover, account has to be taken of the quickly progressing exhaustion of the American turpentine forests. Hilgard conjures up a future vision of the preparation of camphor from petroleum, which is certainly a distant prospect and not a very credible one at the present time. At any rate, the experiments which have for their object the replacement of camphor by similar materials have much more chance of being realised.

In an appendix to the paper, Cayla lays stress upon the complete agreement of Hilgard with the views frequently expressed by him (Cayla), to which we have referred in previous Reports. Cayla regards Hilgard's statements as an indirect confirmation of the conclusions arrived at by Giglioli¹⁾, insofar as the latter particularly referred to the

¹⁾ Report November 1908, 36.

ownness of the wages in Italy and the age of the Italian camphor trees. Cayla is of the same opinion as Beille and Lemaire¹⁾, and also Giglioli, that the camphor production of the future will be established on the basis of making use of the leaves, a process which is already being applied in Formosa and Ceylon. Cayla also calls special attention to the impossibility of synthetic camphor becoming a serious competitor, in view of the present state of the prices; but in regard to this aspect of the matter he thinks that a change might be brought about if coniferous trees yielding turpentine or a similar oil were cultivated in suitable countries, especially in India and in Tonquin.

Cayla²⁾, in his review of Giglioli's book *La canfora italiana* (to which work reference has also been made in our Report³⁾), points out, in opposition to Rivière⁴⁾, that according to the experience of Giglioli it is not necessary to remove the newly-grown leaves from the tree, thereby checking its growth. According to Giglioli, a satisfactory yield of camphor may be obtained from the leaves which have been shed by the tree and have been dried naturally by exposure to the atmosphere, the loss caused by the drying process not being considerable. Artificial desiccation, on the other hand, may cause a loss of camphor-content up to 50 0/0. The suitability of dry leaves for distilling purposes is of interest, because this fact would appear to make it possible to press the leaves for transport to distilleries situated in suitable localities.

Watts and Tempany⁵⁾ have prepared essential oil from the wood, leaves, and twigs of camphor trees grown in the botanical gardens in Dominica, with the following results: —

1. 90 lbs. wood yielded 7,1 fl. oz. of oil; $d_{\frac{27^{\circ}}{16,6^{\circ}}} 0,9012$, $a_D - 13,1^{\circ}$.
2. 33 lbs. leaves and twigs yielded 2,75 fl. oz. of oil; $d_{\frac{27^{\circ}}{16,6^{\circ}}} 0,9024$, $a_D - 18,4^{\circ}$.
3. 29 lbs. leaves and twigs yielded 6,2 fl. oz. of oil; $d_{\frac{27^{\circ}}{16,6^{\circ}}} 0,8987$, $a_D - 19^{\circ}$.

The low yield of oil in the second experiment is attributed by Watts and Tempany to the insufficiency of the condensing apparatus, which caused the loss of a considerable proportion of the oil. All the distillates were clear and colourless, and even during the cooling

¹⁾ Report April 1908, 21; November 1908, 35.

²⁾ Journ. d'Agriculture tropicale 9 (1909), 60.

³⁾ Report November 1908, 28.

⁴⁾ Report November 1908, 36.

⁵⁾ West Indian Bulletin 9 (1908), 275. From a copy kindly sent to us.

no camphor separated from them, which shows that that substance cannot be present in any considerable quantities. Watts and Tempany also state that in his annual Report for 1906¹⁾, Consul Playfair pointed out that the occasional absence of camphor from the oil was ascribed by many theorists to the circumstance that only those camphor trees which grow near the coast attain their full development²⁾, while others declare that male and female camphor-trees grow isolated and that only the former contain camphor. Playfair considers the last-named theory to be incorrect, as the flowers of *Cinnamomum* are polygamous.

Cananga oil. The firmness which characterised the past autumn has now given way to a certain dulness, due to larger supplies, increase of the consignments to European markets, and lack of desire for buying. We have thus been enabled to reduce our quotations somewhat.

From a report by A. W. K. de Jong³⁾ referring to an official visit of inspection made by him to Serang, we take the following information on the production of cananga oil in Java: As the distilleries are at a distance from the plantations, the flowers have to be carted to them. The distilling apparatus into which the flowers (which have previously been pounded) are placed, consists of a copper boiler, fitted with a tube through which water may be poured during the process of distillation. The boiler is connected with the condenser by a copper helm. The copper cooling tube, which has a diameter of about 6", is connected diagonally with a large earthenware pot containing the cooling water, which is not renewed by a constant inflow, but is only replenished when necessary. In the place of Florentine flasks, wine bottles are employed as receivers for the distilled oil. These bottles have a small hole in the kick and are placed in a copper basin filled with water in such a way that the neck of the bottle protrudes above the rim of the basin. The basin, in its turn, is placed on a earthen dish, in order to catch the water that flows over from the copper basin during the process of distillation. This water is returned to the still. Every parcel of flowers is continuously distilled for two days, and during the second day the cooling is only done imperfectly.

In Manila an ylang ylang oil is prepared from cananga flowers which is worth ten times as much as the oil prepared in Java from similar flowers, and it would therefore be desirable to ascertain whether the more valuable variety of oil could not also be obtained from the Java flowers by fractionation. The investigations which were set on

¹⁾ Diplomatic and Consular Reports No. 3913, August 1907.

²⁾ Compare Report April 1908, 23.

³⁾ *Teysmannia* 1908, 578. Batavia. From a copy kindly sent to us.

foot by de Jong¹⁾ with this object have been greatly facilitated by the information furnished by Bacon²⁾. The latter has shown that most first-class Manila ylang ylang oils have a sap. no. of above 100, while the second grade, of which the value equals that of cananga oil, always has a sap. no. below 100. De Jong found that fractions of oils distilled in various factories at Serang possessed the following constants: —

Brand	α_D	Sap. no.	Sap. no. after acetylation
A.	— 23° 0'	27,1	76,7
B.	— 28° 30'	24,1	77,8
1.	— 24° 10'	29,1	—
2.	— 29° 45'	33,0	—
3.	— 35° 0'	32,6	—

As the ester and alcohol content of these fractions was much lower than that of the ylang ylang oil itself (which may possibly be due to the insufficient cooling during distillation), de Jong distilled some flowers himself, which he obtained from the neighbourhood of Tjibin-veng and Tjiterep, near Depok. Partly green and immature flowers yielded the following fractions: —

1. α_D — 21° 32'; sap. no. 17,5
2. α_D — 39° ; sap. no. 23,8
3. α_D — 35° 40'; sap. no. 23,0

Red, over-mature flowers also, either distilled whole or after being pounded, produced only fractions with a rotatory power ranging between α_D — 12° 56' and α_D — 35° 0', and a sap. no. between 9 and 17.

Oil from Batavia flowers gave fractions of α_D — 20° 37' to — 38° 0' and sap. no. 33,6 to 37,3. This oil is better than that from the Depok district, and resembles rather the product obtained in Serang.

According to de Jong, the difference in the constitution of the oil depends upon the site of the trees and upon climatic conditions, but it may also be due to minor botanical differences in the trees. Efforts are to be made to obtain seed and seedlings of *Cananga odorata* from the Philippines, and to acclimatise them in Java, in order that the causes of the difference in the constitution of the Philippine and Java oils may hereafter be made clear.

De Jong further lays special stress upon the fact that the volatility of the esters contained in the oils under examination is not greater than that of their other constituents, because the sapon. numbers of the successive fractions show very little variation.

¹⁾ Milit. Tijdschrift 1908, 1. Batavia. From a copy kindly sent to us.

²⁾ Comp. Report November 1908, 128.

We wish to be allowed to offer a few comments upon the interesting researches of the esteemed author: —

Chemically, cananga oil and ylang ylang oil differ in that cananga oil contains fewer esters, fewer alcohols, and more sesquiterpene. According to de Jong, this is due chiefly to the influence of climatic conditions upon the cananga trees. In Java also there are trees of which the flowers have a somewhat different and more agreeable odour, and de Jong was able to obtain flowers from these trees, which are known as *Canangadedes*. From these flowers he obtained an oil of a somewhat higher ester content, but the ester content of ylang ylang oil could not even approximately be reached, because he did not change the distilling process but carried out this distillation also by means of water.

It is possible that climatic conditions have something to do with the matter, but in all probability the mode of manufacture is of greater importance as regards the difference in the two oils. In any case it may be taken for granted that the distillation process followed in Java must result in an oil poor in esters and rich in sesquiterpenes. This is another example of the great differences which may exist in the character of essential oils according to the method of distillation by which they were obtained.

In the first place, flowers used for distilling purposes should never be pounded. There are not many flowers in which such a process can be applied without injuring the quality of the essential oil. In the case of fleshy, juicy flowers, the pounding process may easily give to the oil an additional herbaceous odour. It is true that by pounding the flowers distillation is facilitated and that the yield of oil is increased, but in this particular case it is at the expense of the perfume of the oil. The destruction of the flowers liberates the essential oil from the cellular tissues, and thereby enables those constituents of the oil which are insoluble in water and have a high b. p. — among them especially sesquiterpene — to volatilise more easily, while volatilisation of such constituents from entire flowers is difficult and only possible to a very slight extent. This explains the higher proportion of sesquiterpenes with a high b. p. in cananga oil.

Distillation by water in the case of this oil is also a mistake, because it has a decomposing action upon the esters and because it impedes the evaporation of those parts of the oil which are the most readily soluble in water, especially of benzyl alcohol and of isoeugenol.

The decomposition of the esters is further increased by the long duration of the distilling process, for it is impossible to distil rapidly owing to the totally insufficient means of cooling.

Again, the distillation water should not be returned to the flowers, as it contains acetic acid from the destroyed esters, and, according

to Bacon, also perhaps formic acid, which have an even more decomposing action upon esters than boiling water. Distillation water, which is rich in oil, should be distilled by itself, and all the water which has evaporated from the still should be replaced by pure water. Finally, owing to the weak distillation, the mass of distilling material in the still will generate steam without being thoroughly stirred up and kept in motion. Hence it is probable that parts of the flowers will adhere to the bottom of the still kept hot by the fire, and will burn to it, which would impart to the oil a sharp and more or less acrid odour.

It is very probable that it would be possible to obtain ylang ylang oil from *cananga* flowers in Java if the flowers were not crushed, and if, instead of water distillation, distillation by water-and-steam were applied; in the manner, for instance, in which the Chinese distil the camphor wood in Formosa and the Siamese the fruit of star anise in Tonquin. In such cases quick distillation and consequently an efficient cooling apparatus are necessary; the distillation of one charge of the still should not take more than a few hours.

The principle of distillation by water-and-steam is that the charge in the still rests upon a perforated bottom, between which and the bottom of the still there is water, which is separated from the charge itself by a space in which steam can circulate. The water may be brought to boiling either by heating with fire, or by a closed steam-worm. By means of a tube at the bottom of the still the evaporated water is replaced by pure water during the process of distillation. The quantity of the water of distillation which is collected is a certain indication as to when and how much water should be added to the still. At the end of every distillation the still should be emptied of water.

Prof. Preuss¹⁾ reports that experimental distillations of the flowers of *Cananga odorata* made in New Guinea have yielded highly satisfactory results. The flowers gave 0,98% of oil and there is a prospect that the oil production will increase. A *cananga* oil which has been sent to us from New Guinea for examination, showed the following constants: d_{15° 0,9143, α_D — $21^\circ 20'$, ester no. 24,1; soluble in half its vol. of 95 per cent. alcohol; when the solution is diluted with alcohol of the same strength it becomes turbid.

Caraway Oil. For the present the reports from the producing-districts in Holland agree that the prolonged winter has in no way damaged the plants, but has only retarded their growth, with the result that they promise to develop all the stronger and more vigorous

¹⁾ Berichte d. deutsch. pharm. Ges. 19 (1909), 25.

for the delay. No definite information is yet available as to the extension of the area devoted to caraway-growing, but it is reported that, as compared with 1908, more has been planted in Brabant, Flanders and Zealand, considerably more in Groningen, and one-third more in North Holland. Many farmers are said to have put the whole of their land under caraway. This considerable extension of the area under cultivation is probably to be ascribed to the good prices which were realised last season. The only stocks of caraway are now in the hands of the exporters, and an important decline in the price is all the more improbable for the present because the existing supplies may hardly last until the new crop is on the market. New season's seed for August/September delivery is being offered for the present at about 25 % less than seed for immediate delivery. So far, therefore, the prospects are favourable, and if the anticipations are not dashed to the ground by bad weather in the spring and summer, low caraway oil prices are to be expected next autumn. Until then the market will probably remain approximately as it is now.

Cassia Oil. The expectations expressed in our last Report have even been exceeded by the changes in prices of the article, inasmuch as the quotations for 80 to 85 per cent. oil have since then receded to 3/5, probably in the first place under the pressure of the low rate of exchange for silver. Even at the present time, owing to want of demand, the market wears a thoroughly lifeless aspect, so that we think we are justified in prophesying a further reduction in value.

Oil of Cassie Blossoms. On the subject of the occurrence and cultivation of the two varieties of acacia which yield the oil of cassie flowers, viz., *Acacia Farnesiana* Willd. and *A. Cavenia* Hook. et Arn., we abstract the following particulars from an article by L. Mazuyer¹). The original habitat of the cassie shrub is India, but it is also a native of Angola, Australia, the Sandwich Islands and the Philippines²). It has been introduced by cultivation into Italy, France, Algeria, Egypt and Syria, and the name *Farnesiana* is said to have been derived from the fact that the plant was first grown in the gardens of Farnese. Both varieties of acacia are found in Provence, in France. The flowers of *A. Farnesiana*, known in commerce as *Cassie Ancienne*, have a finer odour and are more expensive (about fr. 5 to 6 per kilo) than those of *A. Cavenia* (about fr. 2 to 3 per kilo). The usual trade name of the latter variety, *Cassie Romaine*, is probably traceable to its having been brought from Italy to Cannes about a century ago. *A. Cavenia* has the advantage of being less

¹) Journ. de la Parfumerie et Savonnerie 21 (1908), 254.

²) With regard to its occurrence in other places (Cuba, New Caledonia, and the Congo State), see our Reports April 1905, 21; April 1907, 27.

sensitive and requiring less care than *A. Farnesiana*, the latter needing careful pruning every year in March, which is not at all necessary in the case of the other plant. Both varieties like a light, sandy granite soil, but they require a warm and sunny situation, protected against the wind, especially the *Mistral*. The mode of cultivation differs, *A. Farnesiana* being raised from seed, *A. Cavenia* from cuttings. In both cases the planting takes place in March. As soon as the plants have struck sufficient root, they are planted out, *A. Farnesiana* at distances of from 2 to 2,5 m., *A. Cavenia* at from 5 to 6 m. Occasionally, *A. Cavenia* is grafted upon *A. Farnesiana*. The plants demand very little manure, and many farmers fertilise them only every other year. The soil also requires little watering, but this must not be omitted altogether.

The cassie shrubs flower in the first summer after their planting-out, but a full crop can only be looked for from the 5th year onwards. The flowering time of *A. Farnesiana* is from September until the end of December, a medium-sized shrub producing during that time about 600 g. of flowers. *A. Cavenia* flowers considerably longer, that is to say, until April or May, and its yield of flowers is frequently more than double that of the quantity above mentioned. The *Cavenia* flowers are frequently used to adulterate the others, which is all the more easily done as they are difficult to distinguish from the flowers of *A. Farnesiana*. We have given detailed information concerning both oils in previous Reports¹⁾.

Chamomile Oil, Roman. H. J. Henderson²⁾ has observed from authentic distillates of *Anthemis nobilis* that, contrary to what is generally stated, the rotation does not lie between $+1$ and $+3^{\circ}$. Three oils, distilled from dry flower heads, were inactive, while of two oils obtained from the entire, green plant, one was inactive, while the other had a dextrorotatory power of $0^{\circ} 30'$. In the case of the last two oils referred to the sap. no. was 283 and 297 respectively, while for the first-named three oils it was respectively 305, 307 and 317, that is to say, higher than has up to the present been indicated for Roman chamomile oil (250 to 300). The acid number of freshly distilled oils ranged up to 4, in the case of a four-year-old oil it was 7,8. This old oil was also less soluble than the fresh distillates, all of which gave a clear solution with 6 vol. of 70 per cent alcohol. Henderson also questions Gildemeister's and Hoffmann's statement that the Roman chamomile grows wild only in a few districts of Western Europe³⁾. According to him the Roman chamo-

¹⁾ Reports April 1901, 18; April 1903, 17; October 1903, 18; April 1904, 23; October 1904, 18; April 1907, 27.

²⁾ Pharmaceutical Journal 81 (1908), 683.

³⁾ Gildemeister and Hoffmann, *The Volatile Oils*, p. 672.

mile is a specifically British plant and, in the wild state, is known as Scottish chamomile. This is, however, incorrect, as the Roman chamomile occurs wild in France, also in Southern Europe, particularly in Italy (hence the name of Roman chamomile), and in Spain.

We may add furthermore to the above statements that we also have frequently examined Roman chamomile oils of the best quality with a rotation below $+1^{\circ}$; these, however, were very rarely inactive, but this point cannot always be determined because of the colour, which is often very dark. The acid numbers found by us lay between 1,5 and 3,5, the saponification numbers between 250 and 300. From 6 to 10 vols. of 70 per cent. alcohol were required to bring about solution, cloudiness occasionally ensueing; all the oils gave clear solutions with 1 to 2 vols. of 80 per cent. alcohol.

Cinnamon Oil, Ceylon. We continue, as before, to devote special interest to the distillation of this important article, and we are able to state with satisfaction that owing to the exquisite quality of our product our sale has experienced a considerable increase. The prices of pure cinnamon oil remain unchanged, and the market for the raw material also has shown but slight fluctuations. The exports of Ceylon cinnamon chips were as follows: —

in 1908	2785824	lbs.
„ 1907	2835936	„
„ 1906	2531614	„
„ 1905	2325514	„

Of this total, Hamburg imported: —

in 1908	about	554400	lbs.
„ 1907	„	473200	„
„ 1906	„	386400	„

Our own consumption in the past year reached about 115000 kilos, that is to say, approximately about one-half of the total quantity imported via Hamburg.

It is remarkable that in 1908, 200878 ounces of cinnamon oil distilled in Ceylon were exported, a figure reached never before, of which over one-half went to England. Compared with 1907, these figures indicate an increase in the exports of over 100%, and the fact that, this notwithstanding, our distillate found a ready sale at full prices, should afford sufficient proof of its superiority.

In considering the export figures of Ceylon oil given above, it should be remembered that within the past year large quantities of cinnamon leaf oil were shipped from Ceylon, and that these are included in the above statistics. The manufacture of the last-named article has been carried on with an intensity that can only be characterised as senseless, no regard having been paid to the very limited consumption.

In an article in *Southall's Report*¹⁾ the just desire is expressed that the Pharmacopœia requirements relating to Ceylon cinnamon oil should be extended so as to include a definite aldehyde content, in order to prevent adulteration by means of artificial cinnamic aldehyde. The cinnamic aldehyde content of normal oils has been ascertained to range between 70 to 71,4 % whereas adulterated oils have been found to contain from 77,6 to 86,4 %. The specific gravity of normal oils moves between 1,012 and 1,023, in adulterated oils it ran from 1,027 up to 1,055.

The observations relating to the specific gravity of alleged authentic oils recorded in this article do not agree with our own findings, which are the result of records of very numerous observations with our own distillates. We have found the specific gravity of normal Ceylon cinnamon oils to vary from 1,023 to 1,040; lower specific gravities may perhaps be due to the use of defective raw material or to unreasonable methods of distillation. According to our experience, the aldehyde content of good Ceylon cinnamon oils ranges from 65 to 76 %.

Cinnamon bark Oil, Seychelles. In completion of what we wrote in our last Report²⁾ with regard to the Seychelles cinnamon oils, we may state that cinnamon trees growing in the Seychelles Islands are said to be originally deriving from Ceylon. It is stated that an inhabitant of the Seychelles brought over a number of young plants from Ceylon. No further trouble was taken with these, yet they flourished greatly and finally began to spread luxuriantly throughout the islands. The trees develop and are replenished very quickly and were used on the Seychelles hitherto merely as fuel. From this it may be surmised that the Seychelles cinnamon tree represents its Ceylon congener in the wild state. This view is confirmed by an article on the oil industry in the Seychelles in the *British and Colonial Druggist*³⁾, from which we quote the following particulars concerning the occurrence and distillation of cinnamon. Cinnamon trees have been growing in the Seychelles for about a century, the seed having been carried thither by birds. In Mahé the trees are found from the highest mountain-districts down to the coast. Occasionally, especially on the borders of the streams, the plant attains enormous dimensions. Fine trees of about one foot diameter produce about 100 lbs. of dry bark, but the smaller plants may also be used for chips. In Ceylon the bark, after having been freed from the epidermis by scraping, is left to ferment overnight in damp sacks, then dried in the shade

¹⁾ Southall's Report 1908, 17. Quoted from Year-Book of Pharmacy 1908, 53.

²⁾ Report November 1908, 41.

³⁾ British and Colonial Druggist 54 (1908), 152.

for two days and finally exposed to the morning sun on two days. In the Seychelles less time and labour are applied to the work. Here it is thought sufficient to leave the unscraped bark of large trees to dry in the sun for three or four days, as experience has proved that the scraping makes no difference to the yield. Experiments with green, half-dried and fully-dried bark have shown that the dried bark gives twice as much oil as does the green, but that the loss in weight during drying is almost in proportion. On the other hand, the oil from the dried bark has a more agreeable odour and a less acrid taste than that from the green. It is said that in January 1908 the oil yield amounted to 9,4 and 9,2 % respectively of the raw material¹⁾. The yield depends upon the season; increasing in March, when the leaves begin to form, and probably continuing to increase from May up to September. Towards the end of the year, under the influence of the rainy season, it attains its maximum. Similar experience has been gained in Ceylon, where the preparation of the bark is begun about three weeks after the setting-in of the rainy season in May or November. As already stated, large plants yield about 100 lbs. of dry bark, but the average yield is only about 20 lbs., not counting the small branches, which contain an equal proportion of oil. At the present time only the wild-growing plant is used, but perhaps the seed may be sown in districts which are unsuitable for more remunerative cultivation. This will have to be done if more factories should be built, as in that case the material available for distillation would be insufficient. Up to the present only one works of this kind is in existence. This has been built in Sans-Souci and has a steam-boiler and a still with a capacity of 4000 liters. The stills formerly used for experimental distillations were only one-quarter that size.

Besides the bark, the leaves have also been distilled for experiments' sake, but their oil has been found to be less valuable than that of the bark. On the other hand, root-oils have not yet been prepared, as the trees are only cut down and not grubbed up.

The hopes which are built upon the pecuniary profit to be derived from the industry appear to us to be exaggerated, if it is thought possible to compete with the cinnamon oils distilled in Europe from Ceylon chips. According to the experience which we have made so far, the quality of the Seychelles oils is very much inferior to that of the former.

¹⁾ Such a high yield would be unique. The best Ceylon cinnamon yields about 1 %, and Seychelles cinnamon is not likely to yield about ten times as much. No doubt the statements made above are due to a printer's error: it was probably intended to read "0,94 and 0,92 %" respectively.

Cinnamon root Oil. A. A. Pilgrim¹⁾ has examined the oil obtained from the green root-bark of *Cinnamomum zeylanicum* Breyne by means of distillation with steam. The oil was a pale yellow liquid, with a strong odour of camphor, while camphor was found separating out of it at ordinary temperature. The following constants were determined: $n_D^{15} 0.99366$ and $\alpha_D + 50.2^\circ$ (?). The constituents of which the presence was determined were: pinene, dipentene, phellandrene, cineol, camphor, eugenol, safrol, caryophyllene and borneol. We may remark on this that the separation of camphor has long been known, and that Holmes²⁾, many years ago, showed that the oil also contains cinnamic aldehyde.

Citronella Oil. As was to be foreseen, the prices of this article have moved in very narrow limits; nominally they remain below 1/- cif. even at the present time, although exporters in Ceylon until quite recently stood out for somewhat higher rates.

The exports from Ceylon amounted to	1276965 lbs. in 1908
against	1230159 „ „ 1907
„	1107655 „ „ 1906
„	1282471 „ „ 1905

The exports from 1 st Jan. to 15 th Feb. 1909 amounted to	126038 lbs.
do.	do. 1908 „ 76291 „
do.	do. 1907 „ 47041 „
do.	do. 1906 „ 116017 „

The above figures show that the excess of exports in the first five or six weeks of the new year is already about 50000 lbs. as compared with the year before, from which it may be concluded that the reports as to scarcity of supplies which periodically reach us from Ceylon are not to be taken very seriously.

At the present time it is difficult to judge what course prices will take within the near future. Although on the one hand the increased exports may give rise to the belief that the consumption of this oil is again on the increase, we have on the other hand to take account of the fact that, because of the severe competition which exists among them, large soap manufacturers, especially in England, no longer consume anything like as large a quantity of citronella oil as in former years. Almost everywhere, slightly scented household soap is being superseded by strongly perfumed cheap toilet soaps — a result of the extremely low-priced synthetic perfumes which in recent times have found more and more favour with the public.

¹⁾ Pharm. Weekblad 46 (1909), 50. Quoted from Chem. Zentralbl. 1909, I. 534.

²⁾ Pharmaceutical Journal 20 (1890), 749. Compare Gildemeister and Hoffmann, *The Volatile Oils*, p. 382.

In these circumstances, we believe that it may be assumed with some certainty that the present prices will not show any serious fluctuation for some months to come. There is absolutely no ground for expecting an advance in prices.

The sale of the highly popular Java citronella oil within the past few months has also been extremely sluggish, and indications are already perceptible of over-production, on the ground of which a prospective decline in prices of this variety is also to be looked for.

As in the case of lemongrass¹⁾, de Jong²⁾ has also conducted experiments on the oil content of the various parts of Java citronella grass (*Andropogon Nardus* Java; *sereh wangi*) in different stages of development, in order to discover which is the most favourable time for distilling. The result was exactly the same as in the case of lemongrass; as the leaf ages the oil content decreases; the sheaths of the leaves and the roots contain much less oil than the leaves themselves. In this case also, de Jong considers it the best plan to cut the grass as soon as four or five leaves have developed. The greater richness in oil of citronella grass as compared with lemongrass was remarkable; the former usually yielded three or four times as much oil as did the latter. As regards the properties of oil from different batches of old leaves, the optical rotation and total geraniol content (= geraniol + citronellal) show only insignificant variations. The rotation varies irregularly; values ranging from $-2^{\circ}7'$ to $-7^{\circ}36'$ being observed in oil from leaves of various ages. The total geraniol content first increases in an ascending scale from the newest up to the oldest leaf and afterwards decreases in a corresponding manner; the lowest value was 85,5%, the highest 93,3%. The results of this investigation induced de Jong to make experiments as to the time required for acetylation, the behaviour of the oil towards acetic anhydride, the volume of acetate of sodium to be added, and the time required for saponification. On the basis of these enquiries de Jong considers that two hours are needed both for acetylation and for saponification, and that for every 20 cc. of oil and acetic anhydride, 2 g. of sodium acetate are required in order to produce accurate results. He concludes this because in his experiments on citronella oils, he obtained the best values by following this method.

The oils examined by de Jong were soluble in three parts of 80 per cent. alcohol; when more than four parts of the solvent were used, turbidity ensued. According to our observations, the Java oils of commerce make a clear solution with 1 to 2 vols. of 80 per cent.

¹⁾ See Report November 1908, 81.

²⁾ *Teysmannia*, 1908. From a copy kindly sent to us.

cohol and more. Only in exceptional cases does the diluted solution
ow opalescence.

In our last April Report¹⁾ we called attention to the occurrence of
extrorotatory citronella oils, a phenomenon which had never previously
been observed. An oil of this kind is also referred to in the Buitenzorg
Annual Report for 1907²⁾. It had an optical rotation of $+0^{\circ}45'$
and a specific gravity of 0,87.

The experimental cultivation of citronella grass in the German
Pacific Islands having been crowned with success, and resulted in
the production of oils of good quality, closely approximating Java oil,
we now gather from a paper read in Berlin by Prof. Preuss³⁾ that
Andropogon Nardus (author?) is to be more extensively cultivated, as
distillation has already been taken up on a large scale. From a
specimen sent for our examination we have been able to satisfy our-
selves of the good quality of the sample distillates. The specimen
examined has the following characteristics: $d_{15^{\circ}}$ 0,8819, α_D $-0^{\circ}46'$,
 $n_{20^{\circ}}$ 1,46278; joint content of geraniol and citronellal 85,9%, soluble
1,3 vols. and more of 80 per cent. alcohol.

Clove Oil. In concordance with the general condition of business,
the sales of this important article dragged greatly, and remained
restricted within the limits of a moderate turnover for consumption.
No factors of any kind were present which might have induced
speculative undertakings, and thus all influence upon the clove
market on the part of our industry was wanting. Particularly severe
price-cutting in clove oil was again to be observed in London, but
this "privilege" of our English colleagues is so generally known that we
do not feel called upon to refer to it again at length on this occasion.
It is not surprising that these cheap "clove oils" should sometimes
exhibit remarkable properties.

As is our custom in our April Report, we will begin by reproducing
the information supplied by the German Consulate at Zanzibar: —

Clove exports from Zanzibar in 1907.

The exports of cloves from Zanzibar were as follows: —

	Weight in pounds	Value in rupees
1904	14502775	4986449
1905	15312952	4306090
1906	15105760	5349545
1907	18214668	5941817

The exports of cloves in 1907 amounted to 39% of the total exports.

¹⁾ Report April 1908, 32.

²⁾ Jaarboek van het Departement van Landbouw in Nederlandsch-Indië 1907, 67.
Batavia 1908.

³⁾ Berichte d. deutsch. pharm. Ges. 19 (1909), 25.

The exports were shipped to: —

	1904	1905	1906	1907
	Weight in pounds			
Europe . . .	7312375	5673319	8939789	10457830
America . . .	2056175	1769860	717909	1102420
Asia . . .	4839524	7810508	5355875	6553453
Africa . . .	94701	59265	92196	100965
	Value in rupees			
Europe . . .	2633787	1676468	3176924	3387448
America . . .	713420	401027	238975	306061
Asia . . .	1601061	2123255	1901368	2215262
Africa . . .	38191	15340	32278	33046

The shipments to the European markets were distributed as follows: —

	1905	1906	1907
	Weight in pounds		
Rotterdam . . .	1814460	1543310	952006
London . . .	2762850	2650919	3298930
Hamburg . . .	633284	3841300	5529050
Marseilles . . .	218750	585760	418850
	Value in rupees		
Rotterdam . . .	554887	557320	295300
London . . .	820638	915629	1112693
Hamburg . . .	181335	1387202	1770961
Marseilles . . .	54230	207338	125867

In addition to Europe, India absorbs a very large part of the clove-exports, viz.: —

	1905	1906	1907
	Value in rupees		
	1985878	1782609	2149154

The respective shares (in percentages) of the countries principally concerned in the trade are as follows: —

	1905	1906	1907
India	46,5	33,3	36,3
Germany	4,2	25,9	29,8
United Kingdom	19,2	17,0	18,7
United States	11,5	5,4	5,1
Holland	13,0	10,0	4,9
France	1,0	3,8	2,1

In this connection it is to be noted, however, that the Customs Statistics indicate Germany as the country of destination of all cloves shipped in German vessels, whereas the B/L is mostly made out "option Rotterdam-London". London is the World's market for cloves, and the major part of the cloves alleged to be shipped to Germany does not go to Hamburg, but to London.

A table of the clove crops of the last ten years (each crop covers the twelvemonth from August to July) shows the following figures: —

Crop year	Island of Zanzibar	Island of Pemba Frasilah ¹⁾	Total	Average price Rupees
1897/98	44 941	150 703	195 644	6.3.—
1898/99	149 417	481 505	630 982	6.8.9
1899/1900	59 751	206 640	266 381	6.1.—
1900/01	37 567	201 192	238 759	7.—.—
1901/02	43 626	321 599	365 225	6.6.6
1902/03	175 420	251 780	427 200	6.8.6
1903/04	28 369	96 792	125 161	13.4.—
1904/05	76 860	675 683	755 543	9.5.6
1905/06	181 536	109 931	291 467	11.14.3
1906/07	55 833	202 633	259 466	13.—.—

Average yield of each crop: 355 582 frasilah; average price of the last 10 crops: 8.9.3 rupees.

This price only applies to Pemba cloves; Zanzibar cloves are a little dearer.

No exact census has been taken of the clove-trees in the two islands, but from fairly reliable data it is estimated that, in round figures, there are 2 000 000 trees in Zanzibar and 3 000 000 in Pemba. The Government owns on its own plantations in Zanzibar about 130 000 trees, in Pemba 26 000 trees. Taking bearing and non-bearing trees together, one frasilah of cloves gathered represents the produce of 20.9 trees in Zanzibar, and, in round figures, of 10 trees in Pemba.

The last crop of the Government plantations yielded in round figures 7680 frasilah in Zanzibar and 4596 in Pemba.

The calculation of average yields is made extraordinarily difficult by the unusually heavy fluctuations in the output of the several plantations. A further factor in the uncertainty is that in years of an abundant crop, part of the trees cannot be picked at all on account of want of labourers.

Generally speaking, the want of sufficient labourers to harvest the clove crop has a disturbing effect upon the further development of this cultivation, and has driven the prices up to a considerable extent. Whereas, for example, the price formerly paid for gathering the cloves was 4 pesa per pishi (measure of capacity) of cloves, as much as 9 pesa had to be paid at the beginning of the last crop. Taking an average of 8 pesa, the wages paid for gathering come to 2¹/₂ rupees per frasilah. About 20 pishi (= 50 to 60 lbs.) of green cloves equal one frasilah of dried cloves.

Last year about 1200 labourers from British East Africa were brought to Pemba by the Government, and it is reported that about 300 men came to Pemba from Zanzibar to gather cloves. In spite of this it is said to have been impossible to pick the whole of the crop.

The exports of clove stems amounted to: —

	1905	1906	1907
	Weight in lbs.		
Europe	3 777 062	2 317 305	2 055 415
Asia	63 835	63 056	48 125
America	149 426	—	179 900
Africa	—	2 065	—

¹⁾ 1 frasilah = 35 lbs. avoirdupois.

	1905	1906	1907
		Value in rupees	
Europe	285 818	222 608	190 197
Asia	3 622	6 831	4 708
America	9 680	—	15 060
Africa	—	285	—

As in the preceding season, almost the whole of the exports of the current year went to Hamburg, the value sent to that port being 175 648 rupees out of a total of 209 965 rupees.

The prices of cloves in Hamburg have shown a continued falling tendency since last October (when the highest point [108 marks] was reached), and when in the first half of February not less than 9500 bales were brought to market in Zanzibar, they dropped to 88 marks. In London and Amsterdam the quotations were for the time less advantageous, but these variations are fairly well counter-balanced by differences to the detriment of Hamburg at other times.

The estimate expressed in our November Report as to the yield of the clove crop in Zanzibar appears to have been taken too low rather than too high. It is now shown that the total production of the harvest will far exceed 90000 bales, inasmuch as the shipments already known of exceed 100000 bales. In well-informed circles a crop of, say, 130000 bales is even talked of, and although this figure may be put a little too high, because doubtless old stocks in warehouse have been counted in with the new crop, that fact in no way alters the decisive character of the total figures. The comparatively high prices of the past few months may therefore legitimately be put down to the usual manœuvring of the bull party, whose influence upon the course of the market is unmistakable even at the present time.

In the year 1908, in sympathy with the diminished demand, only about 767 500 kilos of clove stems were imported via Hamburg,

compared with about	1 200 000	kilos in	1907
„	850 000	„	1906
„	1 230 000	„	1905
„	333 000	„	1904.

After slight movements upwards and downwards the prices receded from 32 marks per 100 kilos to about 27 marks to 28 marks per 100 kilos, but in the course of the past few weeks the market has shown a somewhat firmer tone.

From the residue of the distillation *in vacuo* of the sesquiterpenic parts of oil of clove stems (free from eugenol) E. Deussen¹⁾ has isolated about 0,1% of an amorphous body, unsoluble in alcohol and melting at about 146°, to which he ascribes the formula (C₂₁H₃₀O)₅.

¹⁾ Berl. Berichte 42 (1909), 380, 680.

Condurango bark Oil. In an exhaustive paper on the chemistry of condurango bark, K. Kubler¹⁾ also describes the essential oil which was obtained to the extent of 0,3 0/0, by subjecting the essential extract to distillation by water vapour. The oil is yellow and possesses an intense, not unpleasantly aromatic, slightly pungent odour, b. p. 140°(?), d_{18° 0,9741, $[\alpha]_D + 6,724^\circ$. By treating it with a 3 0/0 soda solution he succeeded in isolating about 30 0/0 of a neutral, pure constituent of pleasant aromatic odour (b. p. 225°; d 0,927; $[\alpha]_D + 19,56^\circ$) and an acid constituent, which congealed in crystalline form and consisted of a mixture of the higher fatty acids.

Copaiba Balsam Oil. E. J. Parry²⁾ calls attention to the fact that many so-called copaiba oils are found in commerce at the present time which (although they conform to the requirements of the British Pharmacopœia), prove, when subjected to closer examination, to be merely a mixture of African copaiba balsam oil and of gurjun balsam oil, in suitable proportions. One such oil had the following constants: d_{15° 0,902, $a_D - 14^\circ 30'$, soluble in 95 per cent. alcohol. It consisted almost entirely of sesquiterpenes. In acetic acid solution it gave with nitric acid the deep violet colour characteristic of gurjun balsam oil, and when it was fractionated, dextrorotatory portions were also obtained. It gave no crystalline compound with hydrochloric acid, but only an oil of a deep violet-blue colour.

Evans³⁾ has examined a series of copaiba balsams of various origin, in the course of which he made certain observations on the oil content, rotation of the oil, and the acid no. of the residual resin after distillation by water vapour, which are set forth in the subjoined table:

	Oil content	a_D of the oil	Acid no. of the resin
Pará (Maranham) balsam	27 to 40 0/0	$-8^\circ 40'$ to $-17^\circ 14'$	124 to 150,4
Maracaibo balsam	35 to 46 0/0	$-2^\circ 32'$ to $-9^\circ 50'$	132,8 to 156
Carthagená balsam	56 0/0	$-16^\circ 30'$	151,8
	64 0/0	-18°	143,4

Of 19 balsams under examination, one gave a faint gurjun balsam reaction, while two others probably contained small quantities of colophony.

Utz⁴⁾ has published an article on the value of the various colour reactions in the determination of gurjun balsam in copaiba balsam.

¹⁾ Arch. der Pharm. 246 (1908), 658.

²⁾ Chemist and Druggist 74 (1909), 270.

³⁾ Evans' Analyt. Report 1907, 18. Quoted from Year-Book of Pharmacy 1908, 58.

⁴⁾ Chem. Rev. der Fett- und Harzind. 15 (1908), 218. Quoted from Chem. Zentralbl. 1908, II. 1212.

According to him, most of these reactions are useless; only that of Dodge and Olcott, and Turner's test are said to yield unimpeachable results. According to Dodge and Olcott, 4 to 6 drops of concentrated nitric acid are added to a solution of 4 drops of copaiba balsam in 15 cc. of glacial acetic acid. Pure copaiba balsam remains unchanged; when gurjun balsam is present the glacial acetic acid solution becomes purple. In Turner's reaction, 3 to 4 drops of copaiba balsam are dissolved in 3 cc. of glacial acetic acid, a drop of freshly prepared 10 per cent. sodium nitrite solution is added to the solution and the latter is then very carefully poured upon 2 cc. of concentrated sulphuric acid. In the case of pure copaiba balsam the glacial acetic acid layer remains colourless, while if gurjun balsam is present, the solution gradually turns violet.

We made a control test of the two reactions referred to, and were able, on the whole, to corroborate the statements of Utz. But it must be noted that in Dodge's and Olcott's test the colour occasionally disappears very rapidly, while in the case of Turner's test the minutest care was necessary to carry out the overlaying of the sulphuric acid; otherwise the glacial acetic acid layer, instead of remaining colourless, turned brown very easily.

In connection with this matter we may point out that of the various balsams mentioned in our Report April 1905¹⁾ the Pará balsam, strange to say, gives the gurjun balsam reactions referred to above, so that it is scarcely doubtful that this balsam also was adulterated with gurjun balsam. As already mentioned by us at the time, these balsams had come to us at first hand, and therefore we had no reason at the time of doubting their genuineness, as in most cases adulterations are only resorted to by middlemen. In any case, the last thing that could be surmised was that in South America, the country of origin, gurjun balsam, which is an East Indian product, would have been added, for which reason even the high optical rotation of the balsam did not make us suspicious with regard to its quality. We therefore desire to take this opportunity of correcting our views as to the Pará balsam. We may again quote the constants which it was found to possess: d_{15}° 0,9692, α_D — $41^{\circ} 20'$ acid no. 60,75, sap. no. (cold) 64,72. To water vapour it yielded 62,5% of a yellow oil: d_{15}° 0,9180, α_D — $78^{\circ} 48'$, acid no. 3,14, ester no. 0.

Coriander Oil. Plentiful supplies of this oil were available at unchanged prices; but, should the demand become brisker, it is probable that the quotation will have to be raised, as in that case the supplies will scarcely last until the next crop is available.

¹⁾ Report April 1905, 24.

Douglas fir Oil. The Douglas fir (red fir), which ranks among the most widely-distributed and valuable trees of North America and of the great coniferous forests in the North-Western United States, has the following botanical denominations: *Pseudotsuga mucronata* Sudworth, *P. Douglasii* Carrière, *P. Douglasii taxifolia* Carrière, *P. Douglasii denudata* Carrière, *P. Lindleyana* Carrière, *P. taxifolia* Britton, *P. Douglasii* var. *glauca* Mayr, *P. taxifolia* var. *elongata* Lemmon, *Pinus taxifolia* Lambert, *P. Douglasii* D. Don., *P. canadensis* B. Hooker, *P. Douglasii* var. *taxifolia* Antoine, *P. Douglasii* var. *brevibracteata* Antoine, *Abies taxifolia* Poiret, *A. mucronata* Rafinesque, *A. mucronata* var. *palustris* Rafinesque, *A. Douglasii* Lindley, *A. Douglasii* var. *taxifolia* Loudon, *Picea Douglasii* Link, *Picea Douglasii* Bertrand, *Tsuga Douglasii* Carrière, *T. Douglasii fastigata* Carrière, *T. Lindleyana* Roezl.

The oil, obtained by T. C. Frye, of Washington, from the fresh needles and twigs of small trees and from the undergrowth to the extent of 0,8 to 1 0/0, is yellowish-green and has an odour reminding of limonene. It was investigated by J. W. Brandel in collaboration with M. Sweet¹⁾ and its constants were determined as follows: $d_{23^{\circ}}$ 0,8680, n_D^{20} — 62,5°, acid no. 0, sapon. no. 86,6 corresponding to 30,3 0/0 of bornyl acetate, sapon. no. after acetylation 92,1, from which a content of 32,2 0/0 bornyl acetate, equivalent to 25,3 0/0 of free borneol was erroneously calculated. In reality the bornyl acetate content was 34,6 0/0 or 27,18 0/0 of free borneol. No aldehydes could be traced by means of bisulphite. Fractionation of the oil showed it to consist chiefly of terpenes. The lower fractions, which had a pinene-like odour, yielded no nitroso-chloride. The fraction which boiled between 175 and 176° had a limonene-like odour, but (no doubt owing to the small quantity available), no tetrabromide could be obtained from it. The fractions boiling between 161 and 169° formed the chief part of the oil and contained camphene, m. p. 47°. The residue of distillation (b. p. above 190°) was saponified, whereupon the principal part boiled between 180 and 205°. As shown by the oxidation into camphor, (m. p. 171°; oxime m. p. 113°) it contained borneol. The higher boiling parts were of a deep-green colour.

Elemi Oil. Properly speaking, the name Elemi appertains only to the balsam from *Canarium luzonicum*, which is produced exclusively in the Philippines, and from which it is possible to obtain from 25 to 30 0/0 of essential oil. But occasionally the name is also applied to similar balsams of other derivation, the name of the country of origin being added in that case. Thus, the Imperial Institute has recently had an opportunity of investigating so called "African Elemi", and the following particulars are published as to the result of the examination.

¹⁾ Pharm. Review 26 (1908), 326.

Elemi from Southern Nigeria, of which the botanical origin is unknown, varied in colour from white to pale yellow and yellowish green; it was of fairly solid consistency, and mixed with brown spots and vegetable residue.

A sample gave 0,6% of ash, acid no. 55,3, sap. no. 71,9, the essential oil yield amounted to 8,1%. This oil was of a straw yellow colour and contained ample proportions of phellandrene. The following constants are recorded: $d_{15^{\circ}}$ 0,8686, specific rotation in a 100 mm. tube $+ 50^{\circ} 30'$. A second sample gave 0,53% ash, acid no. 37,8, sap. no. 46,2; it contained 4,4% of essential oil.

Uganda elemi, from *Canarium Schweinfurthii* was white to pale yellow and contained a considerable admixture of dark spots and wood, giving it a dirty appearance. The resin contained 0,3% ash; acid no. 29,4, sap. no. 44,8 (both of these determined from a clean, picked sample). Steam distillation of this sample yielded 11,2% of a pale, straw-coloured oil ($d_{15^{\circ}}$ 0,8451; $\alpha_D([\alpha]_D?) + 79^{\circ} 20'$) containing a large proportion of phellandrene.

According to these data, African elemi generally resembles Manila elemi, but it yields a much smaller proportion of volatile oil than does the latter. Possibly, if African elemi were carefully gathered and treated, it might compete with Manila elemi, but as the demand is only small it might be difficult to find an outlet for large quantities, should they be brought to market.

Essential Oils, Sicilian and Calabrian.

In accordance with our usual custom, we subjoin the report of our friend, Mr. Eduardo Jacob of Messina, to which reference has already been made in the preface.

Anyone who to-day on board of a rapid vessel passes through the Straits of Messina, will behold, as formerly, on the one side the smiling green chain of the Pelorian hills, while upon the other there rises majestically the forest-crowned mass of the Aspromonte. As in former times, so to-day, both shores appear to be adorned with a gay wreath of towns and villages, which impress their charming imprint upon the Straits of Messina. But, alas! when on the one or the other side the vessel closely approaches the shore! Where once stood flourishing cities, rich villages, and the smiling country seats of the wealthy of this beautiful corner of the earth, we now only behold confused masses of ruins; jagged remains of broken walls point towards the skies; churches, theatres, palaces, dwelling houses, even the lowly huts of the peasants, have fallen into dust and ruin, and beneath them, throughout the district, from 100 000 to 200 000 human beings lie buried, while the unfortunate survivors have fled from their in-

hospitable native land, and only a few of them, clinging lovingly to the soil upon which they were born, have established miserable new dwellings for themselves in huts made of branches or boards.

In the early morn of 28th December 1908 a terrific earthquake, the centre of which happened to be exactly within the sphere of the Straits of Messina, destroyed this beautiful region. At the very first shock, all that had been built up by the inhabitants in the course of centuries of endeavour, was almost levelled to the ground in the short space of a few seconds, and more than half of the population was swept away by the terrible forces of Nature.

Messina and Reggio have been completely destroyed; in neither town a single house is left standing which affords safe shelter to its inhabitants. Both cities were the offspring of ancient Greek culture; in former ages both were the emporia of the World's commerce of those days; and although in the course of the centuries they had gradually lost their international commercial pre-eminence, yet a flourishing traffic had been maintained in both places, especially in Messina, up to the present day. Among its other branches of trade, Messina — as is well known — held the chief place in the export of Sicilian and Calabrian essential oils. From 40 to 50 commercial firms, all possessing more or less capital, had gradually devoted themselves to this branch of business. Messina and Reggio supplied the whole world with the produce of the essential oil factories of Sicily and Calabria. It is therefore only natural that the earthquake of 28th December 1908 and the total destruction of Messina and Reggio, as well as of all the villages encircling the Straits which that calamity carried in its train, will bring about wide-spread changes in the commercial conditions of these essential oils.

Of the 40 or 50 commercial firms which devoted themselves to the essential oil trade, scarcely one-half is in existence at the present time, and these firms, if able to carry on business at all, will not be in a position to remain located in Messina, as the entire city is uninhabitable, and as, moreover, owing to the cessation of the general movement of trade in the port, opportunities for shipping goods to all parts of the world will in future be rare. It follows that within the next few years the essential oil trade will first of all transplant itself to the neighbouring towns of Catania and Palermo. But if the rebuilding of Messina, contrary to expectation, should be accomplished more quickly than is believed to be probable at the present time, there can be no doubt that the leading forces of the essential oil trade will again concentrate in this city, favoured as it is by its geographical situation and its excellent harbour.

With regard to the market position before and since the earthquake, the following is to be stated.

Although this year it is impossible at the present time to give accurate statistical figures, it may be maintained with justice and on good grounds that the export of essential oil in the course of the year 1908 has not only not fallen below that of the previous year, but has even slightly exceeded it. When the time of the new crop was approaching, the stocks of orange and bergamot oils were entirely exhausted, and only small parcels of oil of lemon were still in existence, these being in the hands of a few firm holders. The prospects of the new crop were, generally speaking, very good, and low prices for all kinds of essences were expected for the year 1909. The manufacture of the new season's orange oil had commenced as usual, although with some slight delay, at the beginning of October, and the oil content of the fruit being satisfactory, it yielded a rich output. Consequently prices fell to about 12 marks, a figure which no longer left any profit to the manufacturers, and which caused a partial cessation of the oil production.

This season the manufacture of oils of lemon and bergamot could only be commenced with considerable delay, because the trees had suffered greatly from the drought during the summer, and it was necessary that the fruit should be left to attain a certain size and degree of maturity. Just as the first small consignments of new fruit had been brought to market, the earthquake came and destroyed, at a single blow, all the existing conditions.

As in all previous years, so in the course of the summer and autumn of 1908, a lively business for future delivery in all varieties of essential oils had been developed, and when the time for the production of the new oil had arrived, consumers abroad were waiting anxiously for the new supplies, as the stocks of old oil which remained in their hands had been extremely reduced.

The destruction of the two cities of Messina and Reggio; the absence during many weeks of all detailed news with regard to the fate of the commercial firms which had entered into contracts with other countries; and finally the arrival of the news that most of these firms were no longer in existence and that their proprietors, with the whole of their families, except a few survivors, had met with a violent death, caused a panic in all the consuming countries of the world. This panic was stimulated by the uncertainty as to the legal position in which traders abroad were placed, most foreign firms having purchased oil in Messina and Reggio for forward delivery, and by the complete ignorance prevailing as to the conditions of production in Sicily, as a result of which it was, for example, thought possible that the lemon crop of the whole island might have been destroyed. Consequently, the stocks of oil which still remained in existence abroad were forced up to incredibly high prices, which partly reacted upon our island.

Palermo, the only commercial town in the island which was able to conduct an export business in essential oils in the first three weeks following the disaster, was besieged with orders from all parts, and in order to keep pace with the extraordinary pressure it was compelled to buy up, at ever increasing prices, whatever oil could be found outside the district affected by the earthquake.

Such an unnatural condition of things of course could not continue very long. Lemons are cultivated almost over the entire island of Sicily, and throughout Calabria, whereas the district visited and damaged by the earthquake was comparatively very small. The manufacture of oil of lemon is carried on in almost all places and villages throughout the island where lemons grow. The principal collecting centre for this produce up to the present time was Messina, but the greater part of the oils have always been pressed outside the Messina district. A strong and continued advance in the prices of oil of lemon was therefore almost impossible of realisation, as it was to be expected that the high prices themselves would result in an increased production.

The conditions in respect of orange oil were somewhat more serious. The season for the manufacture of this oil was almost past, the bulk of the manufactured oil was warehoused in Messina and Reggio, and it was therefore to be expected that with the destruction of these cities, considerable quantities of this oil had been lost. Such has in fact been the case. A not unimportant part of the orange oil of the current season is lost, and the quantity of this oil which is still for disposal is perhaps smaller than has generally been the case in previous years at the corresponding time.

But the situation in oil of bergamot especially appeared to be extremely serious and hazardous. The manufacture of this oil had scarcely commenced — in some districts it had not yet been begun at all — when the catastrophe occurred, and the only district in the whole world in which oil of bergamot is produced was in the very centre of the earthquake district, with the exception of a small portion, that is to say the districts of Melito, Bova, and Palizzi, which however have also been severely visited.

Scarcely a house is left standing from Palmi to Melito along the Western coast of Calabria, and in the gorges and valleys of the mountains and the uplands where formerly stood the flourishing little towns of Bagnara, Villa San Giovanni, Acciarello, Catona, Santa Catterina, Sbarre, Pellaro, Lazzaro, and Salino.

The preparation of bergamot oil was carried on in all these places; where but a short time previously diligent workers had pursued their occupations, death and destruction now reigned instead. Almost half the population has perished or received injuries; part of the survivors, panic-stricken, have sought refuge on board of the men-of-war of

different Nations which rushed to the rescue, and have been carried off to Naples, Malta, Palermo, or Genoa, and the remainder were for a long time unable to shake themselves free from the lethargy in which the sudden stroke of nameless ill-fortune had plunged them.

Thus the manufacture of bergamot oil came to a sudden end, even before it had reached its full development.

The dreadful earthquake shocks caused large quantities of the fruit to fall to the ground; this has mostly been left to rot unused. At certain points on the coast line, especially at Pellaro and Lazzaro, the sea broke upon the shore in waves as high as houses, tearing away trees, fruit, men, and beasts. Hence, part of the fruit on the trees has been destroyed before oil could be pressed from it.

While thus, with the exception of a few places, mental torpor and lethargy prevailed all along the Calabrian coast, business men had flocked to the spot from all countries of Europe, but especially from France, intent upon securing their requirements of bergamot oil for the season. Braving considerable privations and dangers, these men penetrated even into the smallest villages, buying up almost at any price every drop of bergamot oil upon which they could lay hands.

This fact again stirred up the dulled spirits of the unhappy people of Southern Calabria, and rendered them accessible once more to human emotions. Where up to the present they had only beheld and mourned death and destruction, the possibility of making good at any rate a portion of their losses again presented itself. The high prices which were paid for the oil by the foreign visitors induced the manufacturers to dig up their pressing-apparatus from the ruins; the labourers to start work again at double or treble their old wages. It is true that owing to scarcity of hands the work could only proceed very slowly and on a small scale, but nevertheless oil was produced, and will continue to be produced until the fruit falls rotten from the trees, and so long as the oil content leaves a profit on the cost of manufacture.

It is of course impossible at the present time to obtain reliable data anywhere, yet I believe that I shall not be far from wrong if I estimate this season's output of bergamot oil at barely one half of the quantity produced under normal conditions.

From the particulars set forth above the following conclusions may perhaps be drawn: —

Bergamot Oil. If indications go for anything, this oil should attain a high price this year, but this, of course, is also contingent upon the greater or less intensity of the demand from abroad during the next few months. The conditions of price of the article during the later months of the year will depend upon whether the fears will

be realised which are already entertained by experienced gardeners as to the result of the forthcoming crop.

The bergamot is an exceedingly sensitive, capricious tree, and the earthquake has had for its sequel a series of exceptionally severe, bleak storms and hurricanes, with snow, hail, and cold, all of which have affected the bergamot trees adversely. The trees have lost all their leaves and, apart from the remnant of fruit which they still carry, are standing bare and stripped, without foliage and without protection for the developing buds. Leaves must form before the trees can flower in the spring; if the flowers should appear on leafless trees, the setting and development of the fruit will be in extreme jeopardy. Experience shows that in such conditions poor harvests, or even crop failures, are the rule.

Lemon Oil. It is certain that an abundant crop of lemons is waiting to be gathered; consequently, unless the market should be exposed to artificial manipulations, the prices this year should not be subjected to unduly great fluctuations. This, of course, does not exclude the possibility that the prices now current may temporarily advance somewhat.

Mandarin Oil. Although very little has been produced this season, prices have remained comparatively low, and even to-day they do not exceed 40 marks per kilo.

Orange Oil, bitter, which was worth 12 marks last December, has since that time advanced considerably; the crop will be smaller than that of the preceding year.

Orange Oil, sweet. As mentioned above, no heavy supplies of this article appear to exist. The manufacturing season must be regarded as closed, and nothing is more likely than that, with some demand, prices may advance by several marks.

In a report by the Messina Chamber of Commerce on the agrumen oils (comprising bergamot, lemon, orange, and mandarin oils) examined between October 1st 1906 and January 30th 1908, E. Berté and G. Romeo¹⁾ give detailed particulars of the tests applied. We need not here enter fully into a description of the various methods used, as we have already dealt with their main features in previous Reports. We will therefore limit ourselves on this occasion to quoting, from the observations of the authors, the limits of value of the various constants.

¹⁾ Annali del Laboratorio chimico della Camera di commercio ed arti della provincia di Messina. Messina 1908. From a copy kindly sent to us.

Lemon oil. $d_{15^{\circ}}$ 0,856 to 0,861.

The rotation varies according to the producing district and the degree of ripeness of the fruit; generally speaking it ranges from $+58$ to $+66^{\circ}$ (20° C.). The fruit known as *Bastardoni* yields an oil of which the rotation occasionally falls below $+56^{\circ}$.

Evaporation residue 2 to 3,5 ‰; in the case of oil pressed by mechanical means up to 5 ‰.

The citral content varies, according to the methods employed, from 4 to 7,5 ‰.

Beginning of boiling at 175° .

Bergamot oil. $d_{15^{\circ}}$ 0,880 to 0,887; up to a certain degree the sp. gr. is in direct proportion to the ester content. n_D $+7$ to $+25^{\circ}$; usually between $+10$ and $+20^{\circ}$.

Acid content (calculated as acetic acid) 0,15 to 0,2 ‰; in the case of old oils up to 4 ‰.

Ester content 33 to 44 ‰.

Evaporation residue 5 to 6 ‰.

Solubility: Pure bergamot oil dissolves in half its volume of 90 p. c. alcohol, most samples are soluble in their own vol. of 80 per cent. alcohol, the last-named degree of solubility indicates an oil of good quality¹⁾.

Beginning of boiling at 180° (normal press.) equal to 72° (20 mm. press.).

In order to detect the presence of French or American oil of turpentine, Berté and Romeo recommend that the first two fractions of 5 cc. each of 30 cc. oil be distilled off under reduced pressure, and that they be then tested in order to ascertain whether the first fraction has a higher rotatory power than the second. Further, the mean rotation of the two fractions should bear a definite relation to that of the original oil. This relation should alter with the rotation of the oil, and a table is given (compare original report), setting forth particulars under this head.

The following bergamot oils are of inferior quality:

a) The oil obtained from unripe windfalls (*bergamottella*). This oil is known as *nero di bergamotto*. It has a rather unpleasant, pungent odour, a dark colour and a high specific gravity; $d_{15^{\circ}}$ 0,890 to 0,896.

Ester content between 20 and 35 ‰.

b) Distilled oil. This is obtained from the dregs (*feccie di bergamotto*) by distillation with water vapour. It is colourless or yellowish; $d_{15^{\circ}}$ about 0,865; ester content 3 to 6 ‰.

¹⁾ Of the many oils of the highest quality which we have examined in our laboratories, the minority were soluble in 1 vol. of 80 ‰ alcohol. Compare Report November 1908, 60.

Mandarin oil. $d_{15^{\circ}}$ 0,854 to 0,858. $n_D + 67$ to $+ 73^{\circ}$.

n_D of the first half of the distillate averages 3° more than n_D of the original oil.

Orange oil, bitter. $d_{15^{\circ}}$ 0,852 to 0,856. $n_{D20^{\circ}} + 88$ to $+ 96^{\circ}$.

n_D of the first half of the distillate at least 3° higher than n_D of the original oil.

Orange oil, sweet¹⁾. $d_{15^{\circ}}$ 0,847 to 0,852 $n_{D20^{\circ}} + 96$ to $+ 98^{\circ}$.

n_D of the first half of the distillate at least $1^{\circ} 30'$ higher than n_D of the original oil.

Beginning of boiling at 176 to 177° (normal press.); 79 to 81° (20 to 30 mm. press.).

Lemon Oil. When criticizing the Swiss Pharmacopœia²⁾ we pointed out, *inter alia*, that the statements there as to the determination of boiling points were insufficient. In order to obtain correct results, it ought to have been laid down that the entire mercury column must be surrounded by the vapours of the liquid. Fleissig³⁾, by a series of most careful researches, has now experimentally established what are the differences shown in the case of oil of lemon according to whether the mercury column has or has not been wholly exposed to the vapours. He found that a thermometer protruding from the flask registered up to $5,5^{\circ}$ less than one wholly exposed to steam, and that the requirement of the Pharm. Helv. IV that not more than 30% of the oil of lemon must pass over at 170° , is fulfilled only in the latter case. As a result, he arrives at our own conclusion, that either a shortened thermometer must be used or the necessary corrections must be carried out. Fleissig also points out that the barometric pressure should be taken into account. The difference in the boiling point of water at Basle and St. Moritz, for instance, amounts to $5,3^{\circ}$.

Sophisticators have taken advantage of the enormous advance in the price of oil of lemon to throw upon the market oils which are adulterated to an almost incredible extent. E. J. Parry⁴⁾ reports on a whole series of such oils of lemon, the chief adulterants of which were mineral oil, castor oil, turpentine oil and also the terpenes of oil of lemon. Upon evaporation the samples adulterated with mineral oil left a residue of 30 to 50% (specific gravity 0,878) showing the characteristics of paraffin. Normal oil of lemon leaves a residue

¹⁾ For the properties of this, and of bitter orange oil, as determined in our laboratories, see Report October 1906, 35.

²⁾ Report April 1908, 127.

³⁾ Schweiz. Wochenschr. f. Chem. and Pharm. 1909, No. 5. From a copy kindly sent to us.

⁴⁾ Chemist and Druggist 74 (1909), 121.

of only 2,3 to 3,5⁰/₀, so that the enormous proportion of the residue in the oils under notice affords a clue to the degree of sophistication. The castor oil was identified directly by its constants and its insolubility in petroleum ether, and in the samples adulterated with turpentine oil the addition was revealed at once when the optical behaviour of the first 10⁰/₀ of the distillate was examined. For, whereas in the case of normal oils the difference in the rotation of the original sample as compared with the first 10⁰/₀ of its distillate should be at most 5⁰, the values in this case differed by about 30⁰. The addition of lemon oil terpenes reduced the specific gravity from 0,852 to 0,856, besides reducing the citral content.

Orange Oil. The examination of 17 samples of oil of sweet orange, some of which were adulterated, caused E. Dowzard¹⁾ to express himself on the subject of the limits of value applying to the constants of sweet and bitter oils respectively. In this paper Dowzard arrives at the same conclusions which have been formed by ourselves. Having published our results at the time²⁾, a reference to our former statements will now suffice.

Eucalyptus Oil. Oil of the Globulus variety as well as the ordinary Australian oil containing phellandrene was offered plentifully, but we do not believe that satisfactory transactions have been concluded, as the demand has only been of a very restricted character. Large stocks appear to have accumulated at all the principal trading centres, for which reason we regard a fall in the prices within the near future as extremely probable. Oil from *Eucalyptus maculata* var. *citriodora* has been more frequently asked for than it used to be. This oil is particularly esteemed on account of its high citronellal content, and the arrival of several important consignments has made it possible to satisfy the demand.

In the tenth part of the work edited by J. H. Maiden under the title *A critical revision of the genus Eucalyptus*³⁾, a book to which we have already made repeated reference⁴⁾, the following eucalyptus varieties are discussed: —

Eucalyptus piperita Sm. [synonymum: *Metrosideros aromatica* Salisb.].
Eucalyptus Sieberiana F. v. M.

¹⁾ Americ. Journ. of Pharm. 80 (1908), 474.

²⁾ Report October 1906, 35.

³⁾ Sydney 1908.

⁴⁾ Comp. Reports October 1903, 37; October 1904, 39; April 1905, 37; October 1905, 33; April 1906, 35; October 1907, 53; April 1908, 54.

Eucalyptus Consideniana Maiden.

Eucalyptus haemastoma Sm. [synonyma: *E. micrantha* D. C., *E. signata* F. v. M.].

Eucalyptus siderophloia Benth. [synonyma: *E. fibrosa* F. v. M., *E. ornata* Sieb.].

Eucalyptus Boormani Deane et Maiden.

Eucalyptus leptophleba F. v. M. [synonymum: *E. drepanophylla* F. v. M.].

Eucalyptus Behriana F. v. M. [synonymum: *E. pruinosa* Behr, non Schauer].

Eucalyptus populifolia Hook. [Synonyma: *E. micrantha* A. Cunn., non D. C., *E. populnea* F. v. M., *E. largiflorens* F. v. M., var. *parviflora* Benth., *E. bicolor* A. Cunn., var. *parviflora* F. v. M., *E. polyanthemus* Schauer, var. *populifolia* F. v. M.]

Eucalyptus Bowmani F. v. M.

A eucalyptus oil forwarded to the Botanical Institute at Buitenzorg¹⁾ which had been distilled by Dr. Carthaus in the Tengger Mountains of Java, showed d_{26}° 0,996 (?) and $\alpha_D + 4^{\circ} 18'$. At 150° the oil began to boil, up to 200° , 77 % had passed over, and from 200 to 240° , 16 %. The oil is said to consist principally of cineol.

In connection with the above we may refer to two eucalyptus oils which had also been produced in the Tengger Hills and which were sent to us by Dr. Carthaus in 1907. The first of these (which Dr. Carthaus surmises to have been derived from *Eucalyptus crebra*), was brownish yellow. It contained only a small proportion of cineol, and, besides this, phellandrene and cuminaldehyde (aromadendral?); d_{15}° 0,9036, $\alpha_D - 20^{\circ} 56'$, cloudy solution with 5 to 6 vol. of 80 % alcohol.

The second oil was derived from a long-leaved species, said to be *E. piperita* (?) and had a golden-yellow colour; d_{15}° 0,8974, $\alpha_D - 28^{\circ} 26'$. This oil gave a cloudy solution with about 8 vol. 80 per cent. alcohol; the solution in 90 per cent. alcohol, which is clear at first, opalesces when more than 1 vol. of the solvent is added. Cuminaldehyde (aromadendral?) and a great deal of phellandrene were found to be among the constituents; the sample was too small to allow of the determination of cineol. In the case of both oils the presence of phellandrene is evident already from the odour.

E. F. Harrison²⁾ reports on a South African Globulus oil, produced by the Transvaal Eucalyptus Oil Co. of Johannesburg. This sample

¹⁾ Jaarboek van het Departement van Landbouw in Nederlandsch-Indië 1907, 66. Batavia 1908.

²⁾ Pharmaceutical Journal 82 (1909), 4.

had a specific gravity of 0,9227 (15,5°) and an optical rotation of $+3^{\circ}17'$. No phellandrene could be detected in it; on the other hand, it contained much cineol, the phosphoric acid process indicating a content of not less than 83,7 per cent. of this constituent.

Fennel Oil. The sluggish demand has induced the Galician fennel dealers to lower their previously exaggerated pretensions; hence, in the course of the closing months of last year, a very brisk trade ensued, so that it was possible to use considerable quantities for distilling purposes. The animated business transactions were impeded now and then by serious differences in the quality of the material, which, however, appear to have been mostly settled to the disadvantage of the suppliers. In view of the peculiarities of the people who occupy themselves with the exportation of fennel in Galicia, the minutest circumspection is needed in the agreements as to quality and delivery. Other supplies of fennel than the Galician did not affect our industry in the course of the past half year.

Geranium Oil. Considering the unsatisfactory state of the demand in the past year on the one hand, and on the other the fact that, in 1908, 46 600 kilos of Algerian geranium oil were cleared by the customs as compared with 38 700 kilos in 1907, it is not surprising that there has still been no improvement in the value. True, there was no lack of sensational rumours of unfavourable prospects due to bad weather-conditions and impending restriction of culture, but all these and similar tactics failed to draw the market from its state of indifference. Within the last few weeks the producers have been more accommodating than ever before and have tried to find buyers of large parcels for future delivery at the ridiculously low prices now ruling.

The commercial position of Réunion geranium oil is still more distressful. As is well known, this variety is less used in the manufacture of toilet-soaps than is the African kind, because owing to its characteristic odour as well as on account of its other properties it is not suitable for all purposes. We have already had occasion before now to point out that the World's annual consumption, which is estimated by the Syndicate at 30 000 kilos, is actually far from reaching that figure, and we are able to confirm this assertion as the result of more recently received information. Seeing that notwithstanding this, the oil continues to be produced regardless of the demand, it is not surprising that within the last few years the prices have receded by one-half and that every hope of a return of the good old days is vanishing. The well-known "Syndicat de St. Pierre" continues to hold aloof from the market altogether, in the expectation of "better prices"; such, at any rate, is a statement of the *Bulletin commercial de l'Île de la Réunion* of December 30th 1908.

It would be interesting to know what is the quantity still remaining in the hands of this Association, and upon what factors, with the present hopeless outlook for the article, the hopes of an improvement in prices are founded.

The following figures show the course of prices and the quantities exported during the last eight years: —

In 1901	exports	totalled	13953	kilos,	the	price	was	about	fr.	43
1902	"	"	17193	"	"	"	"	"	"	36
1903	"	"	25323	"	"	"	"	"	"	29
1904	"	"	27660	"	"	"	"	"	"	27
1905	"	"	38334	"	"	"	"	"	"	24
1906	"	"	31645	"	"	"	"	"	"	22
1907	"	"	31247	"	"	"	"	"	"	21
1908	"	"	34360	"	"	"	"	"	"	20

In January of the present year a few transactions for future delivery were even put through at about 19 fr. The quality of the shipments during the past year does not call for comment.

In the course of the last few months the market in East Indian geranium oil has been fairly animated. The favourable reports of the forthcoming distillation, mentioned in our last Report, were revoked as far back as the month of November, and thenceforward the cif. quotations for palmarosa oil advanced from about 5/3 to about 7/-, but the latter figure appears to indicate high-water-mark for the present. It is said that in the producing districts severe fever-epidemics have decimated the ranks of the coolies engaged for cutting the grass, so that in many regions manufacturing has been interrupted. Ginger-grass oil of unimpeachable quality is hardly being offered at all, hence a great scarcity may occur shortly.

In one of our earlier Reports¹⁾ we have already called attention to the occurrence in American peppermint oils of dimethyl sulphide $(CH_3)_2S$, at the same time giving some details as to the reactions for the determination of this compound. Recently we have also succeeded in detecting the presence of this body in Réunion, as well as in African, oil of geranium.

On the occasion of working up a large parcel of Réunion oil we obtained from the first runnings a fraction with a b. p. of 30 to 60°, which possessed in a marked degree the unpleasant odour of dimethyl sulphide. By dint of repeated careful fractionation, pure dimethyl sulphide, b. p. 37°, was recovered from this fraction. It was identified

¹⁾ Report October 1896, 58.

by the well-known reactions with chloride of mercury, and chloride of platinum. The presence of dimethyl sulphide in African oil was confirmed in a similar manner.

Mr. J. H. Burkill, of the Indian Museum, Calcutta, who had already on a former occasion¹⁾ been kind enough to send us oil distilled from *Cymbopogon Martini* Stapf. (*Andropogon Schoenanthus* Flück. & Hanb., non L.) has again had the courtesy to forward us nine similar oils, eight of which, upon closer examination, proved to be palmarosa oils, while the ninth was an oil of gingergrass. The oils specified in the subjoined table under nos. 1 to 5 are of special interest because they were personally collected at the stills by Burkill in several parts of the Central Provinces and hence must be regarded as unquestionably genuine samples.

Distillates of *Cymbopogon Martini* Stapf.

No.	Ver-nacular name	Origin, Province	d ₁₅ ^o	α _D	n _D 20 ^o	Acid no.	Ester no.	Total Geraniol	Solubility in 70 p. c. alcohol
1.	"Motia"	Deogaon	0,8895	+ 0° 16'	1,47 274	1,8	40,3	92,65	1,7 vol.
2.	"	Behali	0,8891	+ 0° 15'	1,47 313	1,5	34,7	94,65	1,6 "
3.	"	Lebada	0,8895	+ 0° 17'	1,47 254	1,6	38,4	93,4	1,7 "
4.	"	Arnadi	0,8889	+ 0° 55'	1,47 264	1,0	39,4	93,9	1,8 "
5.	"	Balkhara	0,8924	+ 1° 18'	1,47 313	0,9	38,9	92,0	1,7 "
6.	"	Ellichpore	0,8896	+ 0° 12'	1,47 392	1,1	12,4	90,9	1,7 "
7.	"	"	0,8911	+ 0° 12'	1,47 313	0,8	40,0	93,9	1,7 "
8.	"	"	0,8917	— 0° 53'	1,47 470	0,8	17,3	87,9	1,6 "
9.	"Sofia"	"	0,9024	+ 3° 54'	1,47 163	2,3	15,0	89,5	1,7 "

According to this table, all the "Motia" oils proved to be good palmarosa oils of normal characteristics. Their geraniol content is very high; in fact, it only falls below 90% in sample no. 8. The oils differ to some slight degree from each other as regards odour, but they nevertheless all possess a pure palmarosa character, and in this respect also they answer all requirements, except sample no. 6, which has a slightly musty odour. Sample no. 9, "Sofia" is a gingergrass oil of exquisite quality, and therefore its composition differs entirely from that of the "Motia" oils. As we have already on previous occasions²⁾ reported in detail on this point, as well as on the botanical origin of the "Motia" and "Sofia oils", a reference to these Reports will now suffice.

Gurjun balsam Oil. A balsam sent to us under the designation of Cochin Wood Oil was absolutely identical with ordinary gurjun balsam, both as regards colour and odour, and as regards its constants. The

¹⁾ Report April 1907, 58.

²⁾ Reports April 1904, 56; October 1904, 52; April 1905, 55; April 1907, 30.

alsam, which was of a brown colour, with a greenish fluorescence, showed the following characteristics: d_{15}° 0,9633, α_D — $37^{\circ} 30'$, n_{D20}° 1,51236, acid no. 7,8, ester no. 2,9. Even with absolute alcohol it only gives a cloudy solution, from which flocculent separation takes place quickly. When the sample was distilled by steam it yielded 69,9% of a lemon-yellow oil, possessing the following properties: d_{15}° 0,9248, α_D — $61^{\circ} 48'$, n_{D20}° 1,50252, acid no. 0, ester no. 1,6; soluble in 9 vols. and more of 95 per cent. alcohol. At normal pressure (741 mm.) 86% passed over between 260 and 265° , and 6% between 265 and 269° .

Oil from *Helichrysum angustifolium* Sweet. From Hungary we received a sample of oil which showed almost similar characteristics as did an oil from the same plant distilled by ourselves and described by us at the time¹). It possessed the following constants: d_{15}° 0,9084, α_D + $4^{\circ} 25'$, n_{D20}° 1,47450, ester no. 134,0, soluble in 6 to 7 vols. and more of 85 per cent. alcohol. The slight differences between this oil and that previously examined are possibly due to differences in the state of maturity of the plant or in the method of distillation.

Oil of *Illicium religiosum*. Some time ago we had an opportunity of investigating Japanese star anise oil²) distilled from the fruit of *Illicium religiosum* Sieb., a drug which was formerly often used as an adulterant of genuine star anise. The oil differs from oil of Chinese star anise chiefly in the fact that, unlike the latter, it contains scarcely any anethol, while its principal constituent is safrol of which Chinese oil contains only traces. The Japanese oil, therefore, congeals in the freezing mixture only at about -18° , with separation of safrol. When subjected to fractional distillation under 3,5 mm. pressure, also a fraction containing cineol was obtained. With concentrated resorcinol solution this fraction gave the characteristic cineol-resorcinol combination. Another fraction appeared to contain linalool, but owing to the smallness of the sample available the presence of this could not be ascertained with certainty. The constants of the oil were as follows: d_{15}° 0,9848, α_D — $0^{\circ} 50'$, acid no. 1,8, ester no. 12,9, soluble in 5 to 6 vols. and more of 80 per cent. alcohol, paraffin being separated.

Behaviour on fractionating (3,5 mm. pressure): —

1.	to 40°	21,6%	α_D + $6^{\circ} 20'$	Cineol fraction.
2.	40 to 65°	8,0%	α_D + $1^{\circ} 14'$	Contains linalool (?).
3.	65 to 79°	17,2%	α_D — 5°	} Safrol fractions.
4.	79 to 83°	32,0%	α_D — $4^{\circ} 6'$	
5.	83 to 90°	4,6%	α_D — $3^{\circ} 30'$	
6.	Residue	16,6%		

¹) Report October 1903, 76.

²) Report October 1902, 80.

Juniper Oil, empyreumatic (Cade Oil). In our last Report¹⁾ we referred at length to a paper by Pépin on the origin, preparation and examination of cade oil. A publication of this kind deserves the warmer welcome because it tends to revive the interest in this oil. If less has been heard in recent years of the excellent action of this oil in skin-diseases, which has been praised by leading dermatologists, the reason is simply that the adulteration of cade oil has lately assumed incredible dimensions and that a really pure article is nowadays almost the exception. In most cases, therefore, it may be taken for granted that the non-success of cade oil which has been observed in dermatological practice is due to its admixtures. Probably even it often happens that other empyreumatic distillates are used in lieu of cade oil, and with the present insufficient knowledge of the properties and composition of the article it is difficult to recognise such substitutes invariably and with certainty. This matter was all the more perplexing because up to now it has been almost impossible to obtain a really authentic material which would serve as a standard in judging cade oil. It is therefore undoubtedly to Pépin's credit that he should try to re-establish the reputation of genuine cade oil by showing, from material distilled by himself, what should be the requirements of a genuine oil.

We have followed the whole question with great interest and have at once taken the necessary steps to procure a guaranteed pure cade oil, which we have recently begun to list. We also refer to this oil here in order that, by bringing it to the notice of the widest possible circle, we may induce dermatologists to experiment again with pure cade oil with renewed confidence.

The examination of a sample of the oil gave the following results: d_{15}° 1,0309, acid content (calculated for acetic acid) 0,64 %, permanently clearly soluble in any proportion of chloroform and anilin. In the case of solutions in ether, benzene and glacial acetic acid, which at first are also clear in any proportion, precipitates occur after some lapse of time. An equal volume of oil and of 90 or 95 per cent. alcohol is required for solution, and here the solution remains clear when further quantities of the solvent are added, but in both cases a flocculent separation occurs after some time. In boiling, the oil behaved as follows: —

760 mm.		3 mm.	
150 to 300°	about 55 %	80 to 150°	about 53 %
300 „ 350°	„ 12 %	150 „ 175°	„ 12 %
Residue	„ 31 %	Residue	„ 32 %

¹⁾ Report November 1908, 24.

The discrepancies existing between our own and Pépin's observations are explainable by the fact that so far only few oils have been examined, and that certain fluctuations of course also occur in pure oils. A considerable quantity of experimental material and further research into the whole question will be necessary before it becomes possible to establish really authoritative constants for each oil. The marked difference between Pépin's record of the behaviour on boiling and our own is due to the different manner in which the thermometer was handled. While in the case of our investigations the whole of the mercury column was exposed to the vapours, Pépin placed his thermometer so that 230° was above the stopper. When operating in this manner, we found the fraction passing over between 150° and 300° to be 60% .

Kobushi Oil. A kobushi oil examined by Y. Asahina and H. Nakamura¹⁾, which had been distilled in the Japanese province of Shizuoka from one year old twigs, showed in some respects considerable differences from the kobushi oils which had been examined so far²⁾. This oil was bright yellow and had an odour reminding of citral. $d_{15^{\circ}} 0,892$; $n_D + 6^{\circ} 8'$; acid no. 4,3; sap. no. 19,1; sap. no. after acetylation 56,48, soluble in 1,4 vol. of 85 per cent. alcohol, further addition of the solvent produced opalescence. It was found to possess the following constituents: citral (6 to 7% , α -citryl- β -naphthocinchonic acid, m. p. 197 to 200°), eugenol (benzoyl compound, m. p. 69°), cineol (cineol iodide, m. p. 112 to 113° , cineolic acid, m. p. 195°) and, as principal constituent, methylchavicol which yielded homoanisic acid (m. p. 84 to 85°) and anisic acid (m. p. 184°) when oxidised with permanganate of potash. According to the authors, the oil may also contain pinene, because the fraction boiling between 150 and 160° yielded traces of a nitroso-chloride which could not be more closely characterised on account of its scarcity. The authors found the following acids: caprinic acid (silver salt, readily soluble in hot water, $38,52\%$ Ag) and oleic acid (silver salt, insoluble in hot water, soluble in hot alcohol, $27,54\%$ Ag). It is worthy of note that the oil examined by Asahina and Nakamura contained no anethol, a substance of which the presence in kobushi oil has been proved quite clearly by ourselves as well as by Charabot and Laloue. We identified the anethol direct by its m. p. 22 to 23° . Asahina and Nakamura employed for purposes of identification picric acid among other substances, whereas according to Bruni and Tornani³⁾

¹⁾ According to the Journ. of the Pharm. Soc. of Japan, No. 322, Dec. 1908. Tokyo.

²⁾ Report October 1903, 78; April 1908, 61.

³⁾ Compare the abstract in Chem. Zentralbl. 1904, II. 954.

this reacts only with bodies having propenyl side-chains, but not with bodies having allyl side-chains. Whereas anethol combines with picric acid in orange-red needles, melting at 68 to 70°, the experiment in the case of all fractions of the oil in question remained without any result whatever.

The absence of anethol, however, is not the only respect in which this oil differs from the samples previously examined. It is also lighter and, opposite to the others, dextrorotatory. Furthermore, the occurrence of eugenol and of the acids referred to above are new features in kobushi oil. It is possible that these variations may be partly accounted for by the conditions under which the distilling material was grown, or by the fact that in the distillation of the oils previously examined a larger proportion of leaves was used than in the case of the sample referred to above.

The statement may also be of interest that the flower-buds and the stalks of *Magnolia Kobus* are an old-fashioned Japanese remedy, which was formerly used against headache, under the name of *Shin-i*.

Oil of Laurel leaves. In addition to the oils distilled in France and Germany, the produce of other countries is now also frequently seen on the market, oils of quite suitable quality being offered from the Mediterranean Islands and from Palestine in particular. The following table gives a graphic view of the characteristics of the various oils:

	d ₁₅ ^o	α _D	n _D ²⁰ ^o	Acid no.	Ester no.	Ester no. after acet.	Solubility
German and French	0,915 to 0,932	—15° to —18°	1,469 to 1,477	up to 2,0	28 to 43	58,3 to 77,7	in 1,3 vol. 80 p. c. alc., some (esp. French) samples in 3 to 10 vol. 70 p. c. alc.
Fiume . . .	0,9281	—13° 52'	1,47156	1,0	31,9		in 2,5 vol. 70 p. c. alc. and more
Corfu	0,9177 to 0,9211	—16° 40' to —21° 40'	1,46862 to 1,47107	up to 1,5	29,8 to 43,8	36,2 to 82,5	in 1 volume 80 p. c. alc., mostly in 3 to 6 vol. 70 p. c. alc.
Cyprus . . .	0,9405	—5° 40'	1,47372	1,6	25,3	95,6	in 2 to 3 vol. 70 p. c. alc. and more
Palestine . .	0,916 to 0,924	—14° to —21°	1,46516 to 1,46575	up to 2,2	21 to 49	43,2 to 81,4	in 1 to 2 vol. 80 p. c. alc., some in 4 to 7 vol. 70 p. c. alc.
Asia Minor .	0,9268	—15° 50'	1,46575	0,8	34,8	60,1	in 1 volume 80 p. c. alc. and more

Lavender Oil. Business in lavender oil had dragged on quite lifelessly during the past five months. As a result of the bad state of trade, buyers showed themselves extremely reticent, but on the

other hand many producers also refused to sell at the low prices which ruled as a consequence of the abundant crop, and kept back their holdings in the hope of a more profitable opportunity of disposing of them. These expectations, however, have not been realised, or, leaving out of account a slight improvement of the market which made itself felt in the beginning of February, when several firms in Grasse were compelled to cover themselves, and which has again been perceptible lately, the article is, generally speaking, thoroughly neglected. In the principal producing districts the winter was exceptionally severe, and the snowfall the heaviest on record for forty years. In some parts of these districts, people were cut off from the outer world for a long time and several parcels of lavender oil which we had on the way suffered considerable delay in transport. As a result of timely and important purchases, we have been enabled to reduce our quotations to some slight extent.

We have previously referred to the observations of Birckenstock¹⁾ on the effects exerted by the hybridising of *Lavandula vera* D. C. and *L. Spica* D. C. upon the properties and the constitution of the essential oil.

The paper of H. L. Visser on the examination of lavender oils, to which reference was made in our last Report²⁾, has called forth some comments by W. J. de Maar³⁾. The latter agrees with Visser that the Dutch Pharmacopœia has fixed too low a maximum limit (0,890) for the specific gravity of the oil, but he does not believe that by demanding a minimum content of 35 % of linalyl acetate the Pharmacopœia will exclude the most of the lavender oils of commerce, because he himself has had no difficulty in obtaining oils which fulfil this condition, provided he paid corresponding prices. De Maar expresses his astonishment that Visser's experiences in regard to this matter should have been so unsatisfactory, and that, in spite of the abnormal properties of the commercial oils examined, Visser should have had no doubts as to their purity.

We should not again have referred to Visser's paper, were it not that that investigator had in the meantime published in the *Pharm. Weekblad* a contribution⁴⁾ in which, among other things, he seeks to controvert our criticism. Visser maintains here that we have misinterpreted the object of his article, as the publication of his researches was merely intended to show that lavender oils occur in the wholesale

¹⁾ Report October 1906, 43.

²⁾ Report November 1908, 80.

³⁾ Pharm. Weekblad 45 (1908), 1536. From a copy kindly sent to us.

⁴⁾ Pharm. Weekblad 46 (1909), 39.

trade which do not satisfy the requirements of the Dutch Pharmacopœia. No objection whatever could have been raised against a publication having such a purpose, if Visser had not made the mistake of regarding adulterated oils as pure, and of drawing conclusions from these erroneous premisses. In order to avoid confusion, it was obviously necessary to correct such a mistake, although it can be understood that the reason why Visser believed the oils to be pure was that they were alleged to come from reliable sources. One of the oils in question was even reputed to have been obtained from us as "Ol. lavand. Ph. Ned. IV", but its characteristics were such ($d_{15^{\circ}} 0,900$, $\alpha_D - 13,5^{\circ}$, ester content 38,9 %) that we feel bound here to give an explicit denial to this assertion. We declare that lavender oils of such a description would not be supplied, and have never been supplied, by us. Unfortunately the firm to whom we are said to have supplied the oil had nothing left of it, so that we are unable to clear up the misunderstanding involved in the assertion.

With the object of increasing the interest in lavender growing in the South of France, L. Lamothe has published a new article entitled "*la Lavande*"¹⁾ which, broadly, contains all the information which we have already quoted from this author's publications on previous occasions²⁾. A new statement is that in the principal lavender growing districts a syndicate of distillers has been formed for the purpose of undertaking the cultivation and distillation of lavender on rational lines. Since last year this syndicate has already acquired a number of modern stills, and it is said to have produced oils with an ester-content of from 40 to 57 %. Its sphere of activity extends over the entire region of the Upper Drôme, the Hautes-Alpes and the Basses-Alpes, which is known to produce by far the best oils. Adjoining this district is that of the Italian Alps, with a lavender oil of inferior quality, and, as a third zone of cultivation, the region of the Lower Drôme and the Vaucluse.

The output of oil in the various Cantons is somewhat as follows: La Motte-Chalançon and Séderon, 4500 kilos each; Luc-en-Diois 3000 kilos; Bourdeaux, Saillans, and Rémuzat each 2500 kilos; Dieulefit, Nyons and Buis-les-Baronnies each 2000 kilos oil of the best lavender; the Cantons of Pierrelatte, Grignan, and St. Paul-Trois-Châteaux together 2500 kilos of lavandin oil³⁾. As already stated in our last Report⁴⁾, the total output of the Department of the Drôme is therefore on the average 28000 kilos of oil.

¹⁾ La Parfumerie Moderne 1 (1908), 3.

²⁾ Report November 1908, 76.

³⁾ Report October 1906, 44.

⁴⁾ Report November 1908, 78.

The principal centres of production in the department of the Basses-Alpes, with a total yield of about 12000 kilos of oil of exquisite quality, are the Lure Mountain chain, together with Cruis, Mallefoûgasse, St.-Etienne, Banon, Forcalquier, Châteauneuf, Valbelle, Sisteron, the district of Barrême, Clumac, Lambruisse, Tortonne, Castellane, and Digne.

Lemongrass Oil. Since we last reported on this article, the quotations have moved round about 2 d. per oz., with slight upward and downward fluctuations. An attempt to engineer a demand for lemongrass oil on the occasion of the Sicilian disaster, on the ground that this oil forms the raw material for citral, must be pronounced a complete failure. Considerable stocks of lemongrass oil are held in Europe, and as, in spite of the low values, the growers in India continue cheerfully to produce in spite of the low value, there seems for the present to be no prospect of more remunerative prices.

In our previous Report (p. 82) we stated that, according to de Jong's researches, Java lemongrass oil, although giving a clear solution with 2 parts of 70 per cent. alcohol immediately after distillation, becomes less soluble already after a few days; and that de Jong is of opinion that this change is due to the polymerisation of a terpene.

F. Watts and H. A. Tempny¹⁾ have experienced similar results with oils distilled in the West Indies. They also attribute this phenomenon to the polymerisation of a hydrocarbon which, they think, is perhaps identical with myrcene.

As we have repeatedly stated in our Reports, the same difficulty of solubility is manifested by the lemongrass oils distilled in Brazil, Mexico, Africa etc., all of which are currently termed "West Indian" lemongrass oils. This want of solubility finally becomes so pronounced that even solutions of the oil in absolute alcohol, which are clear at first, become cloudy when more of the solvent is added. On the other hand, the so-called Malabar, Cochin, or Travancore lemongrass oils (= "East Indian" lemongrass oil) remain readily and clearly soluble in 70 per cent. alcohol even a long time after distillation. Stapf²⁾ has ascertained that the difference in the behaviour of the oils is due to the fact that the plants of origin are not the same, the Malabar oil being obtained from *Cymbopogon flexuosus* Stapf, and the West Indian oil from *C. citratus* Stapf. According to Watts and Tempny³⁾, the Botanic Stations on the Leeward islands are engaged in the experimental cultivation of *Cymbopogon flexuosus* (Cochin grass) in order to

¹⁾ West Indian Bulletin 9 (1908), 265. From a copy kindly sent to us.

²⁾ Comp. Report April 1907, 58.

³⁾ West Indian Bull. 9 (1908), 267.

make it possible to obtain a lemongrass oil which should be equal in every respect to the Malabar oil. The grass grows well there, and the fact that four samples of oil from Cochin grass grown in Antigua and Montserrat did not as yet reach the high citral content desired (they contained respectively 53, 63, 64 and 68 %) is ascribed by Watts and Tempny to the insufficient degree of ripeness of the grass, experiments with "West Indian" grass having shown that not only the oil yield but also the citral content of the oil increase in proportion to the ripeness of the grass. 72,5 kilos of a grass grown in Antigua, three months old, yielded upon distillation 139 cc. of oil with 58 % of citral, while an equal weight of one year old grass yielded 206 cc. of oil with 69 % of citral. The most favourable conditions for harvesting Cochin grass are to be determined still. From the results hitherto obtained by the experiment station it appears that from two to three crops may be gathered in the course of the year, each cutting producing from 6000 to 8000 lbs. of grass per acre. The oil yield was found to be from 0,2 to 0,26 %.

Two illustrations of the distilling process given in the *Bulletin* are evidently intended to represent a general indication of the mode of distilling volatile oils, the various parts shown (still, rising tube, condenser, and receiver) not being given to scale.

As mentioned in our last Report¹⁾, experiments similar to those of Watts and Tempny have been made in Barbados with most favourable results. A lemongrass grown by the Government laboratory in that island from Cochin seed yielded a readily soluble oil and very rich in citral.

To a previous note²⁾ on an oil said to be derived from *Andropogon Schoenanthus* which was examined in the Government laboratory at Antigua and behaved altogether abnormally, being in no way ascribable as Palmarosa oil, but rather resembled lemongrass oil, we are now able to add the statement that the oil in question was the product of a lemongrass four years old, which had never previously been cut. We take this statement from a comparative table dealing with a series of West Indian lemongrass oils, which has been prepared by Watts and Tempny.

We quote from a paper read in Berlin by Prof. Preuss³⁾ the statement that the experimental cultivation of *Andropogon citratus* (author?) in New Guinea has shown profitable results, and that the distillation of lemongrass oil is now to be commenced there on an

¹⁾ Report November 1908, 82.

²⁾ Report October 1902, 50.

³⁾ Berichte d. deutsch. pharm. Ges. 19 (1909), 25.

extensive scale. In the course of the last few years we have frequently had occasion to examine similar lemongrass oils from the German Colonies in the Pacific and have found them to equal, as regards their properties, the oils which we have received from the West Indies, Mexico, Brazil, Java, Africa, etc. As their aldehyde content is fairly high, the New Guinea oils will be very suitable for the preparation of citral. Four samples of New Guinea oils showed the following constants: —

	I	II	III	IV
$n_{D}^{15^{\circ}}$	0,8850	0,8852	0,8923	0,8810
α_D	— $0^{\circ} 15'$	— $0^{\circ} 22'$	— $1^{\circ} 15'$	— $0^{\circ} 11'$
Citral content:	78 %	78 %	65 %	76 %

Solubility: All the oils are insoluble in 70 per cent. alcohol; with 80 and 90 per cent. and even with absolute alcohol they give at first clear solutions, but when more of the solvent is added cloudiness or opalescence sets in.

Another lemongrass oil which was sent to us for report from Uganda (British East Africa) possessed exactly similar properties: $n_{D}^{15^{\circ}}$ 0,8703, $\alpha_D \pm 0^{\circ}$, citral content 67 per cent., insoluble in 70 and 80 per cent. alcohol; with 90 per cent. and with absolute alcohol it dissolved clear at first, becoming turbid when more solvent was added.

Limette Oil. We learn from the *Pharmaceutical Journal*¹⁾ that in the island of Dominica the lime industry has reached an extraordinary development. In 1907 the crop of fruit reached 272 229 barrels, an increase of 32 000 barrels as compared with 1906. The area under cultivation has been greatly extended, and it is estimated that in the year just closed from 400 to 450 acres were under cultivation. Lime-growing is also steadily increasing in the island of Montserrat, where it has again reached its former importance. The fruit is chiefly grown for its juice, limette oil being a by-product.

Linaloe oil. The price-conditions of this article persistently decline to assume a more favourable aspect. It is true that the importers have occasionally cleared out small parcels at less than the market-rate, and that more favourable purchases could at times be made, especially in Paris, but when, owing to the catastrophe in Southern Italy, an extraordinary demand set in for linalyl acetate as a substitute for bergamot oil, the quotations rushed up to the extent of 200 %. But now that the effects of the earthquake have been to some extent overcome, and bergamot oil is again available, it is probable that there will be no further call upon the linaloe oil market for this particular purpose. Hence the position is likely to become quieter again before long.

¹⁾ *Pharmaceutical Journal* 82 (1909), 19.

It will be remembered that a few years ago¹⁾ we reported repeatedly on dextrorotatory linaloe oils which, as regard their other characteristics, behaved like normal oils. The constants then observed lay within the following limits: d_{15° 0,8783 to 0,8816, $\alpha_D + 2^\circ 54'$ to $+ 8^\circ$, n_{D20° 1,46149 to 1,46209, acid no. 1,2 to 1,7, ester no. 3,74 to 20,0, soluble in 1,6 to 2,0 vols. and more of 70 per cent. alcohol. Similar oils were afterwards observed by Parry and Bennett²⁾ and by Simmons³⁾. Closer examination of one specimen has shown to us that as regards their chemical composition these oils differ from the lævorotatory oils which had been found in commerce up to that time, only by their content of d-linalool and l-terpineol (m. p. 35°); for the rest, like the others, they contained geraniol and nerol. From a communication which has appeared in the *Berichte* of Roure-Bertrand Fils⁴⁾ it now appears though as if the question of the origin of these dextrorotatory linaloe oils has been solved, inasmuch as the examination of an authentic oil distilled from the seed of the linaloe tree produced a result identical with that of our examinations referred to above. This oil from seed contained besides l-linalool, l-terpineol, nerol and geraniol, and possessed the following constants: d_{15° 0,8858, $\alpha_{D26^\circ} + 1^\circ 30'$, n_{D18° 1,4655, soluble in 1,5 vol. and more of 70 per cent. alcohol, acid. no. 3,4, sap. no. 34,3 (corresponding to 10,8% $C_{10}H_{17}OCOCH_3$). From these results the authors consider themselves warranted in assuming that the seed of the linaloe-tree yields a dextrorotatory oil, and that the oils referred to above must therefore be regarded as linaloe seed oils. The future will show whether this assumption is correct. We will only, on this occasion, observe in parentheses that in the year 1899 we received from Venezuela an oil said to be prepared from linaloe-seed which possessed the following constants: d_{15° 0,893, $\alpha_D - 2^\circ 26'$, sap. no. 86,2, soluble in 2,5 vols. of 70 per cent. alcohol, producing a slight opalescence with more than 5 vols. We are, however, not in a position to make an authentic statement as to the origin of this oil.

When working-up a considerable parcel of linaloe oil, we obtained, after saponification of the oil with alcoholic potash and subsequent distillation by water vapour, an alcoholic first running, from which after addition of water, we were able to separate an exceptionally light, faintly optically active oil (d_{15° 0,7727; $\alpha_D + 1^\circ 46'$). It commenced to boil at 42° in a moderate vacuum (18 mm. press.) and

¹⁾ Report October 1904, 56; October 1905, 47.

²⁾ Chemist and Druggist 68 (1906), 544; Report October 1906, 47.

³⁾ Chemist and Druggist 68 (1906), 584; Report October 1906, 47.

⁴⁾ Berichte of Roure-Bertrand Fils, October 1908, 18.

distilled at ordinary pressure between 108° and 170° . Its constants, as well as its behaviour when boiled with sodium warranted the assumption that we had here to deal with unsaturated aliphatic hydrocarbons, and the behaviour towards bromine pointed to the same conclusion. By repeated fractionation over sodium under normal pressure we obtained optically inactive fractions of such abnormally low specific gravity that in the circumstances they could only be regarded as hydrocarbons of petroleum. The elementary analysis showed in fact that the portions boiling between 120 and 145° consisted of octylene and nonylene and their isomers. One fraction, possessing the b. p. of octylene and the following constants: $d_{15^{\circ}} 0,7396$, $n_D \pm 0^{\circ}$, $n_{D20^{\circ}} 1,41255$, b. p. 122 to 125° , yielded upon analysis the subjoined values: —

- I. $0,1491$ g. subst.: $0,4645$ g. CO_2 , $0,1931$ g. H_2O .
 II. $0,1663$ „ „ $0,5195$ „ CO_2 , $0,2165$ „ „

	Found	Calculated for C_8H_{16}
	I. II.	
C	$84,96\%$ $85,20\%$	$85,70\%$
H	$14,39\%$ $14,46\%$	$14,28\%$

The physical constants and the analytic values of a fraction with the b. p. of nonylene likewise agreed completely with those of this olefine: $d_{15^{\circ}} 0,7477$, $n_D \pm 0^{\circ}$, $n_{D20^{\circ}} 1,41808$, b. p. 139 to 142° .

$0,1648$ g. subst.: $0,5144$ g. CO_2 , $0,2169$ g. H_2O .

	Found	Calculated for C_9H_{18}
C	$85,13\%$	$85,70\%$
H	$14,62\%$	$14,28\%$

We may leave it an open question whether octylene and nonylene are to be regarded as normal constituents of linaloe oil, or whether hydrocarbons of petroleum were present in these particular fractions; but in any case it is very improbable that such hydrocarbons had been added to the linaloe oil as adulterants, because for this purpose the quantity found present (1 to 2 per cent) would have been too small. Possibly the occurrence of these hydrocarbons in linaloe oil may have been due to the oil having been shipped in dirty tins which had previously contained petroleum. At the same time we may take this opportunity of pointing out that Burgess and Page¹⁾ had already found octylene to be present in oils of lemon and bergamot.

We were further able to determine that in the lowest boiling fractions of linaloe oil there occurs, besides the terpene proper, an olefinic terpene ($\text{C}_{10}\text{H}_{16}$) which is probably identical with myrcene.

¹⁾ Journ. chem. Soc. **85** (1904), 1327; Report April 1905, 31 and 35.

A fraction which served for the purpose of detecting the presence of this body showed the following constants after having been freed from methylheptenone: d_{15° 0,8243, $\alpha_D + 0^\circ 32'$, n_{D20° 1,46476, b. p. 169 to 173° (atmospheric press.), b. p. 63 to 65° (16 mm. press.). Elementary analysis gave the following results: —

0,1744 g. subst.: 0,5628 g. CO_2 , 0,1872 g. H_2O .

Found		Calculated for $\text{C}_{10}\text{H}_{16}$
C	88,01 %	88,23 %
H	11,92 %	11,77 %

The oil under discussion shares with the well-known olefinic terpenes the property of resinifying quickly when left exposed to the air, or when distilled under normal pressure. When re-distilled over sodium the hydrocarbon passed over between 172 to 183° . Under the conditions formulated by Enklaar¹⁾ for the preparation of myrcenol from myrcene, the terpene, when warmed for 3 to 4 hours to 40° with glacial acetic and sulphuric acids, yielded an acetic ester with a b. p. of 80 to 87° (4 mm. press.) from which, upon saponification, there resulted an alcohol possessing the properties of myrcenol²⁾. We determined: b. p. 79 to 83° (3 to 4 mm. press.), d_{15° 0,9061, n_{D20° 1,47995. The alcohol possessed the markedly characteristic and pleasant odour (only distantly reminding of linalool), which also belonged to a preparation of myrcenol made by us for purposes of comparison. Unfortunately, in the case of both preparations we vainly endeavoured to bring to crystallisation the oily phenyl urethanes which had been obtained. A negative result also attended repeated efforts to identify the dihydro-myrcene (which had been obtained from the terpene by reducing it with sodium and alcohol) by the tetrabromo dihydro-myrcene (m. p. 88°) prepared according to Enklaar's directions. The product of reduction possessed the following constants: b. p. 169 to 173° , d_{15° 0,7849, n_{D20° 1,44378, which agree fairly well with those given by Enklaar for dihydro-myrcene.

The terpene which was found in association with the olefinic terpene, and to which reference has been made above, could neither be characterised by a bromine derivative nor by a nitroso-chloride or a nitrite, but the optical rotation $\alpha_D + 8^\circ 41'$ of a fraction boiling between 65 and 72° (16 mm. press.) indicated its presence.

Linaloe Oil, Cayenne. The only fact known up to the present with regard to the chemical composition of Cayenne linaloe oil was that its chief ingredient consisted of linalool. In a paper by Theulier³⁾

¹⁾ Compare Enklaar: *Over Ocimeen en Myrcen*. Dissert. Utrecht 1905; Report April 1906, 109.

²⁾ Ibidem.

³⁾ Rev. gén. de Chim. III. 6 (1900), 262; Report April 1901, 40.

which appeared some years ago, Cayenne linaloe oil was stated to differ from the Mexican variety by the absence of methyl heptenone, terpineol and geraniol. Having had occasion to examine Cayenne linaloe oil ourselves, we have ascertained that Theulier's observation is incorrect, inasmuch as we succeeded in establishing beyond all doubt the presence in the oil of both d-terpineol (m. p. 35°) and of geraniol. Judging by the odour of the first runnings, however, it must be admitted that methyl heptenone appeared to be absent. We found the oil under examination to possess the following constants: $d_{15^{\circ}}$ 0,8786, n_D^{20} — $12^{\circ} 29'$, sap. no. 4,2 acid no. about 1, soluble in 2 vols. of 70 per cent alcohol.

The oil fractionated by us had been saponified with alcoholic potash from which the alcohol had been removed by distillation by water vapour. Apart from a small quantity of first runnings, the bulk of the oil passed over between 68 and 95° (6 to 7 mm. press.). The fractions with b. p. 68 to 75° containing the linalool were left out of account. For the determination of the terpineol we used a portion of the oil which, after repeated fractionation, passed over between 83 and 88° (7 mm. press.). The mere odour of this showed the presence of terpineol. When inoculated the cooled fraction solidified completely. The crystals, pressed out on porous tiles, melted at 35° and, in their re-melted state, had an optical rotation $n_D + 18^{\circ} 6'$, which proved them to consist of d-terpineol. The phenylurethane obtained from them after treatment with carbanile had, as was expected, the m. p. 111 to 112° . In order to prove the presence of geraniol, a fraction with a b. p. of from 90 to 93° (6 m. m. press.) was heated for several hours on the water bath in benzene solution with phthalic anhydride. From the sodium salt solution of the resulting phthalic ester acid there separated upon saponification and simultaneous steam distillation, an oil with an unmistakable geraniol-like odour. This passed over at from 91 to 92° (5 mm. pressure) and at 227 to 228° under atmospheric pressure and was recognized as geraniol by its specific gravity ($d_{15^{\circ}}$ 0,8820), its optical inactivity, and its odour, as well as by the diphenyl urethane (m. p. 80 to $81,5^{\circ}$). The terpineol content of the oil did not exceed 5% , nor the geraniol content 1% .

Oil of Lovage root, own distillation. After a long interval we have this year again distilled two parcels of oil of lovage from different highly developed roots, one parcel being obtained from fresh Thuringian root of the second year's growth and another from fresh root of the first season, of our own growth. In spite of the difference in the age of the material used, the oils show only unimportant differences in their properties, and a mere enumeration of their constants will therefore be sufficient: —

	Yield	d_{15}°	α_D	n_D^{20}	Acid no.	Ester no.	Ester no. after acet.	Solubility in 80 p. c. alc.
I. Fresh Miltitz root, 1 st year	0,22 %	1,0310	+ 1° 30'	1,55148	5,8	223,5	—	in 2 vols. and more
II. Fresh Thuringian root, 2 nd year	0,55 %	1,0326	+ 0° 46'	1,54944	6,1	224,5	227,8	in 2,5 vol. and more

From the but slight increase in the sap. no. after acetylation of the oil as compared with the original sap. no. we may infer that, besides the esterified alcohol, practically no free alcohol is present.

Matico Oil. We observe from a note by G. Weigel in the *Pharmazeutische Zentralhalle*¹⁾ that there have recently appeared in commerce matico leaves from *Piper Mandoni* D. C. which differ in important particulars from the well-known variety of the drug. They attain a length of from 18 to 20 cm., and even up to 25 cm., and mostly measure from 12 to 15 cm., but often as much as 20 cm., in width. The stalk is strong and very hairy, and the leaf is less acutely pointed than that of the familiar species and is of an oval-ovate or reversed heart shape. On the other hand, genuine matico leaves from *Piper angustifolium* Ruiz et Pavon are narrow and lanceolate, about 15 cm. long and only 4 cm. broad.

We procured a parcel of the *Piper Mandoni* leaves for distilling purposes and obtained from them about 0,8 % of a brownish oil, with a balsamic odour and with the following constants: d_{15}° 0,9360, α_D + 1° 5', n_D^{20} 1,49704, sap. no. 1,8, ester no. 5,1, ester no. after acetylation 46,7, soluble in 6 vols. and more of 70 per cent. alcohol.

Oil of Monarda fistulosa. E. Kremers, in collaboration with N. Wakeman²⁾, has made experiments in the quantitative determination of the oxidase which occurs in the leaves of *Monarda fistulosa*, and which converts into thymoquinone the hydrothymoquinone contained in this plant³⁾, and the two investigators, in connection with these experiments, have made researches on both these combinations. We will only specially mention here that thymoquinone, dissolved in alcohol or limonene, was reduced to thymo-quinohydrone or hydrothymoquinone; for the rest a reference to the original paper must suffice.

Mustard Oil, genuine. We are just now engaged in working up a large parcel of exquisite material and shall shortly be able to replenish our supplies. At the moment we have not yet been able

¹⁾ Pharm. Zentralhalle 49 (1908), 974.

²⁾ Pharm. Review 26 (1908), 314, 329, 364.

³⁾ Comp. Report October 1904, 58.

to cast up our cost price, but we can state even now that no reduction in the quotation is to be thought of, for we are already satisfied with the barest imaginable margin of profit.

Myrtle Oil. Although the oils of myrtle found in commerce are almost exclusively of French and Spanish origin, we have had frequent opportunity, of late years, of investigating oils from other sources, especially from Corsica, Asia Minor and Syria. As a matter of general interest we record below the constants of such oils: —

Oil from	d _{15°}	α _D	n _{D20°}	Acid no.	Ester no.	Ester no. after acet.	Solubility
Corsica . . .	{ 0,8828 0,8868	{ + 26° 46' + 23° 15'	{ 1,46 644 1,46 911	{ 1,0 1,6	{ 13,0 17,1	{ 30,2 38,5	{ in 2,5 vol. } ,, 0,8 ,, } 90 p. c. alc.
Syria	{ 0,8930 0,8985	{ + 14° 30' + 11°	{ — 1,46 417	{ 1,9 —	{ 20,3 26,6	{ 72,0 70,7	{ ,, 5,0 ,, } ,, 1,0 ,, } 80 p. c. alc.
Asia Minor .	{ 0,9138	{ + 10° 42'	{ 1,46 704	{ 1,5	{ 39,4	{ 94,9	{ ,, 0,9 ,, }

In connection herewith we may mention that in the course of our investigations we have also observed small differences in the constants of Spanish and French oils. These are shown in the subjoined table:

	d _{15°}	α _D	n _{D20°}	Acid no.	Ester no.	Ester no. after acet.	Solubility
Spanish oils	{ 0,913 to 0,924	{ + 22° to + 25° 20'	{ 1,467 to 1,470	{ up to 1,7	{ 68 to 83	{ 103 to 117	{ in 1 to 2, rarely up to 5 vol. 80 p. c. alc.
French oils	{ 0,890 to 0,904	{ + 15° to + 23°	{ 1,465 to 1,468	{ up to 1,5	{ 19 to 28	{ 38 to 56	{ in 0,5 vol. 90 p. c. alc., the majority in 5 to 10 vol. 80 p. c. alc.

Neroli Oil. In spite of the unfavourable weather (among the features of which are hail and snow storms), which has prevailed in the South of France during the past month, the orange trees have only suffered very slightly, and from their appearance it is hoped that the crop will be a middling one. The cold weather has greatly retarded the young buds, and the experience of past seasons shows that when the blossoming-period commences late it is comparatively short and consequently never yields a very abundant crop. In any case it may be anticipated that the prices of flowers will be somewhat lower than in 1908 and, presupposing that no continuance of bad weather nullifies all prophecies, neroli oil is also likely to be offered at somewhat more advantageous rates.

A business-friend at Besançon has sent us, by way of a curiosity, an oil of neroli distilled from orange-flowers gathered in the locality. The small sample was of a bright brown colour and possessed a quite agreeable, although not very fine aroma. Apart from a somewhat high acid no., its constants were approximately normal: $d_{15^{\circ}}$ 0,8780, $n_D^{20} + 7^{\circ} 15'$, acid no. 6,1, ester no. 58,4 soluble in 1,3 vol. of 80 per cent alcohol. When more alcohol was added, cloudiness ensued and paraffin was separated.

Nutmeg Oil. In the course of their investigations in the toxic effects of nutmegs (referred to on page 114 of the present Report), F. B. Power and A. H. Salway¹⁾ also deal with the requirements attached to essential oil of nutmeg in certain Pharmacopœias. Of this part of the paper we will only say that Power and Salway rightly regard it as illogical that the German Pharmacopœia should designate essential oil from nutmegs by the name of *Oleum Macidis*, since by mace oil is understood the oil of the nutmeg flower and since the identity of the two oils has not been established. While the American Pharmacopœia originally required the oil to possess a specific gravity of 0,862 to 0,910 at 25°²⁾ the Supplement to that Pharmacopœia demands 0,884 to 0,924³⁾. Power and Salway assume this to be a mistake for 0,864. The requirement of the U. S. Ph. (obviously taken from the British Pharmacopœia), that from 2 to 3 cc. of nutmeg oil must leave no crystalline residue upon evaporation is regarded as unpractical, as normal distillates will often fail to satisfy this demand, because the fractions of the oil with the highest b. p. contain myristic acid. Hence, an oil which unconditionally conforms to the requirements of the U. S. Ph. would consist only of the fractions possessing the lower boiling points.

Orris Oil. We have received the following report from our correspondents: —

At the time of our October report on Florentine orris-root, the price was 62 to 63 marks cif. Hamburg for pickings, and 52 to 53 marks cif. Hamburg for seconds. At that time we estimated the new crop at about 400 tons, but as, owing to the favourable weather conditions prevailing, the supplies came in during a longer period than usual, the actual crop amounts to about 500 tons.

Add to this the remainder of old stocks at the end of September 1908	„ 515 „
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The total supply available for the new campaign was therefore	about 1015 tons.
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The shipments from the end of September 1908 to the end of February 1909 amounted to	„ 265 „
leaving available at present (1st March 1909)	about 750 tons.

¹⁾ Americ. Journ. Pharm. 80 (1908), 568.

²⁾ Report April 1906, 75.

³⁾ Report October 1907, 102.

The exports from the beginning of October up to the end of February (about 265 tons) cannot be called heavy, but just recently numerous orders have been received, particularly from France. Moreover, the scanty yield of the crop in the district of Verona (according to our latest computations it amounted only to about 70 tons, compared with a maximum yield of 600 tons a few years ago), has also influence on the Florentine market. Numerous orders have come in for the latter variety, as a result of which, along with the new crop, the still remaining stocks of Veronese orris root have been exhausted, excepting a small quantity which is in firm hands. This fact has further strengthened the position. Veronese orris of the quality known as "mercantile" was purchasable in October for 35 marks, whereas now the parity of 43 marks cif. Hamburg is being paid. Hence a speculative movement has developed locally in Florentine orris root, and the orders which are coming in are encouraging the dealers and speculators to further purchases, with the result that we are at present compelled to quote 64 marks for Florentine orris in pickings, and 54 marks for seconds, both cif. Hamburg. It will of course depend upon the future demand whether these prices will be maintained or perhaps advance still further. We have already previously stated that of about 515 tons of old stock, about 100 tons are worm-eaten, and it appears that since we wrote the proportion of worm-eaten root has become still larger, for which reason great care is necessary in buying. The yield of the last seven crops has been as follows: —

1902 . .	about 1000 tons,
1903 . .	" 750 "
1904 . .	" 670 "
1905 . .	" 850 "
1906 . .	" 800 "
1907 . .	" 500 "
1908 . .	" 500 "
Total	about 5070 tons,
Average about 725 tons.	

On the other hand, the average annual exports during the past six years, according to our October report, amounted to about 692 tons. In case, therefore, the next succeeding crops should again average only about 500 tons, or even less, as appears likely owing to the reduced planting, this shortage, judging from the statistical position of the article, might easily start a rise in prices, unless the consumption of orris root should fall off owing to the cheapness of ionone, as to which we are, however, unable to form an opinion.

In connection with the concluding sentence of the above review, we may state that, in our opinion, it is true that the competition of cheap violet-scents makes itself felt by restricting business in orris oil, and that he who would build his plans upon a brisker demand during the next months would probably make a miscalculation. Moreover, it is to be remembered that on March 1st the available stock amounted to full 750 tons, that is to say more than an average season's production. Even a restriction of planting is therefore unlikely to have a stiffening effect upon the market position in the near future.

Parsley Oil. As the apiol content of German oils differs from that of French oils of parsley¹⁾, H. Thoms²⁾ had intended to

¹⁾ Comp. Gildemeister and Hoffmann, *The Volatile Oils*, p. 548.

²⁾ Berl. Berichte **36** (1903), 3451; Report April 1904, 67.

determine by cultivation experiments whether external conditions, such as mode of cultivation, climate etc., were of influence in causing this difference. The results of his experiments, which have now been published¹⁾, are interesting in several respects. Of the French seed, which was supplied by us, a portion was immediately distilled (sample no. 1), while the rest was sown at Dahlem in Germany in the spring of 1904. The fruit of this, gathered in the autumn of 1905, was distilled in February 1906 (sample no. 2). As the following table shows, the differences in the composition of the two oils are only slight, but it must be borne in mind that important influences would only be perceptible after repeated cultivation: —

	Sample 1	Sample 2
d_{15}°	1,03	1,07
Terpene content	about 5 %	about 5 %
Acid mixture (chiefly palmitic acid) . . .	0,1746 %	0,876 %
Phenols	0,184 %	2,51 %
Principal fractions at 15 mm. pressure		
a) 160 to 165°	28 %	25 %
b) 165 to 170°	47 %	35 %

The determinations of carbon, hydrogen, and methoxyl showed that in both oils the principal fractions possessed approximately the same composition. In all the four fractions the presence of apiol could be detected, and by brominating, myristicin was found in the form of dibromo myristicin dibromide, while the high values obtained for the methoxyl content further indicated the presence of a phenol ether still richer in methoxyl. In order to determine the character of the last-named body, the fraction was first treated with alcoholic potash and afterwards reduced with sodium in alcoholic solution. But neither from the hydrated phenol which had been obtained by this process (b. p. 156 to 160° at 17 mm. pressure) nor from its methylation product (b. p. 160 to 165° at 19 mm. pressure) could any solid bodies be isolated by cooling. Both substances, however, yielded a nitro product melting at 65°, which proved to be identical with the 1-propyl 2, 3, 5-trimethoxy 4-nitrobenzene already previously obtained from apiol²⁾. Oxidation of the fractions with permanganate, however, threw some light upon the character of the phenol ether in question, for besides yielding myristicin and apiolic acids, this process resulted in the formation, as the principal product, of 2, 3, 4, 5-tetramethoxy benzene carboxylic acid-1, which had already been previously obtained by Bignami and Testoni³⁾ by the oxidation of a fraction of parsley oil. Finally Thoms succeeded, by cooling the fractions with solid carbonic acid, in isolating the phenol-ether itself in solid form. Among its constants the following may be

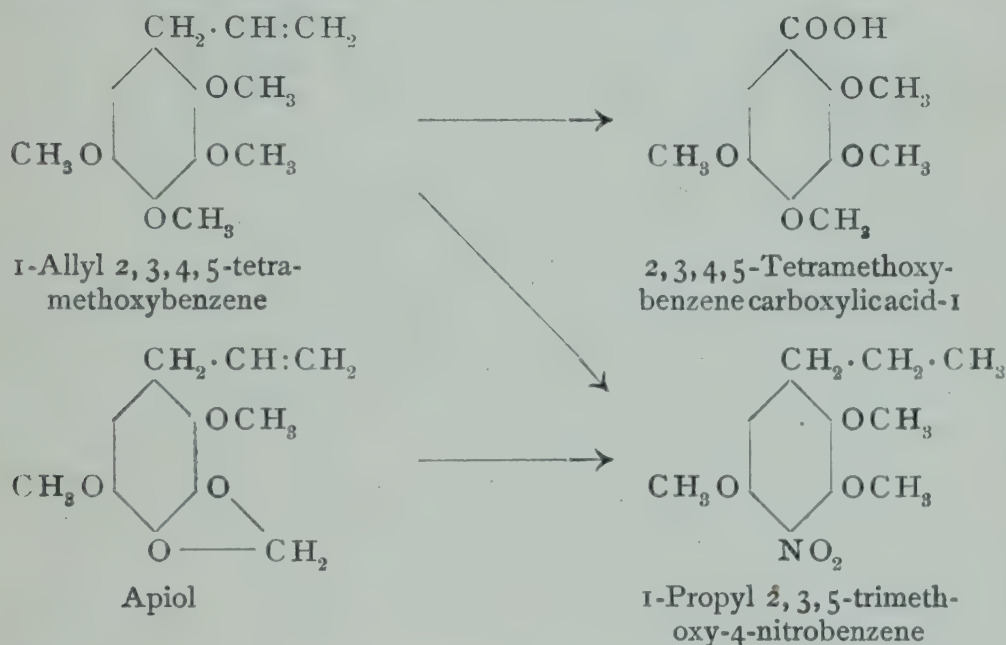
¹⁾ Berl. Berichte 41 (1908), 2753.

²⁾ Berl. Berichte 36 (1903), 1714; Report October 1903, 100.

³⁾ Gazz. chim. ital. 30 (1900), I. 240; Report October 1900, 48.

mentioned: m. p. 25° , d_{25}° 1,087, n_{D25}° 1,51462, mol. refr. found 65,7, calculated 64,77. The pure body also was converted into the acid (m. p. 87°) by oxidation and into the nitrated compound (m. p. 65°) by reduction and subsequent nitration. These facts, together with its behaviour towards alcoholic potash, phloroglucinol and hydrochloric acid, picric acid, or hydrochloric acid, as well as the values ascertained for refraction and dispersion, made it possible to determine its nature as 1-allyl 2,3,4,5-tetramethoxybenzene, a body which has not previously been found in essential oils.

The following formulæ exhibit the connection existing between the combinations in question: —



Patchouli Oil. The value of this oil, which is such an indispensable article in the perfumery trade, has remained entirely unaltered since last October. It has all along been difficult to procure suitable material for distilling purposes, and in face of the keen competition of the cheap, albeit generally thoroughly bad, Indian distillate, the profit on patchouli oil of our own manufacture is being so much reduced that important transactions can only be effected in the case of customers who are really connoisseurs.

In our last Report¹⁾ we published particulars of the examination of a series of patchouli oils which had been sent to us by Dr. de Jong. Roure-Bertrand Fils have obtained a similar collection from Buitenzorg, and they communicate the result of their investigations on these in their *Berichte*²⁾. With one exception these results tally with those obtained by us. The exception is that Messrs. Roure-Bertrand

¹⁾ Report November 1908, 95.

²⁾ Berichte of Roure-Bertrand Fils, October 1908, 27.

Fils found one of the two oils prepared from fresh Java leaves to possess the following constants: $d_{15^{\circ}} 0,9112$, $\alpha_D + 0^{\circ} 52'$, sap. no. 4,1, soluble in 8,5 vols. and more of 90 per cent. alcohol. In our case, both these oils were found to be lævorotatory, to have a higher specific gravity and to be more readily soluble.

From a paper read in Berlin by Prof. Preuss¹⁾ we observe that experimental distillations have been made of wild patchouli plants from New Guinea. The oil yield was 3,75 % and the experiment was so promising that it is intended to commence the cultivation of patchouli there. A similar specimen-distillate examined by us showed the following constants: $d_{15^{\circ}} 0,9847$, $\alpha_D - 58^{\circ} 10'$, sap. no. 1,8, ester no. 8,4, soluble in 0,4 vol. and more of 90 % alcohol.

Peppermint Oil, American. During the last six months the market has offered little of interest, and the prices showed a falling tendency, as the demand has not been proportionate to the supply.

The yield of the 1908 crop was smaller than that of the two preceding years, but the existence of sufficiently large stocks held over from 1906 and 1907 more than compensated for the reduction, and even if in the coming season there should be a further restriction in the laying down of new plantations, there will yet remain quite sufficient oil for disposal.

The farmers are to a large extent losing their interest in cultivation, and it is becoming more difficult every season to find special qualities, as not sufficient new plantations are laid down, and the old plantations, owing to the low market prices, are not attended to and cleaned with sufficient care.

Our stock for the next months to come has been excellently assorted by timely purchases, and we believe that at the prices now prevailing, which are still low, we are justified in advising our clients to supply their wants quickly and plentifully.

Peppermint Oil, French. In their last *Bericht* Roure-Bertrand Fils²⁾ make some statements with regard to observations on peppermint oils from Grasse, which we here reproduce shortly. Two oils distilled in 1907 and 1908 behaved as follows: —

	1907		1908	
	Crude	Rectified	Crude	Rectified
$d_{15^{\circ}}$	0,9210	0,9198	0,9156	0,9159
α_D	$- 13^{\circ} 4'$	$- 17^{\circ} 6'$	$- 15^{\circ} 28'$	$- 16^{\circ} 50'$
Menthyl acetate . .	13,5 %	13,7 %	15,4 %	13,3 %
Total menthol . .	49,8 %	53,5 %	52,2 %	54,9 %

¹⁾ Berichte d. deutsch. pharm. Ges. **19** (1909), 25.

²⁾ Berichte of Roure-Bertrand Fils, October **1908**, 23.

In referring to the differences between Grasse peppermint oil and that of other origin, Roure-Bertrand Fils also call attention to the fact that the Grasse variety would not be admitted by most Pharmacopœias. If the firm should conclude from this that the requirements of the Pharmacopœias have been laid down "without sufficient technical knowledge", such a judgment must be regarded as somewhat too severe. Outside France, French oil does not enter into commerce at all, and it is therefore not surprising if the Pharmacopœias have not paid special attention to it.

As a special peculiarity of the Grasse oil, Roure-Bertrand Fils mention its behaviour in a freezing mixture. Even when cooled down to -17° it was impossible to bring the oil to congealing point, even after inoculating it with menthol. It is hoped that the intended examination of the alcoholic constituents will explain this behaviour of the oil.

To the foregoing we would add that in the case of the highly esteemed English and Saxon oils also crystalline separations frequently only take place after the oils have remained for a long time in the freezing mixture; hence the quantity of crystallisable menthol differs altogether in the oils of various origin, and is not a direct measure of their value. At the same time we refer to our own communications on South French peppermint oils¹⁾, which partly behaved similarly to those examined by Roure-Bertrand Fils. We may further place on record here an observation which we have made concerning the rapid resinification of two oils distilled by ourselves in Barrême. Both oils were examined some weeks after distillation, and at first behaved as follows: —

- | | |
|---|--|
| 1. $d_{15^{\circ}}$ 0,9184; $\alpha_D - 10^{\circ} 44'$; mthl. as ester 12,0 %; total mthl. 50,2 % | $\left. \begin{array}{l} \text{Sol. in 1,1 vol.} \\ 80 \text{ p.c. alc.; with} \\ \text{more than 2,5 to} \\ 3 \text{ vol. pronounc.} \\ \text{opalescence.} \end{array} \right\}$ |
| 2. $d_{15^{\circ}}$ 0,9273; $\alpha_D - 10^{\circ} 56'$; „ „ „ 14,8 %; „ 54,7 % | |

Accidentally the specific gravity was again determined a fortnight afterwards, on which occasion a considerable increase in weight was ascertained. Two following observations, made at intervals of a fortnight each, showed a further increase, which is indicated in the following table: —

	Originally	After a fortnight	After 4 weeks	After 6 weeks
Oil 1. $d_{15^{\circ}}$ 0,9184		0,9191	0,9224	0,9292
„ 2. $d_{15^{\circ}}$ 0,9273		0,9291	0,9322	0,9380

The reason for this is to be found in the fact that the herb had been worked up while it was still quite green. In such a state, readily resinifying constituents pass into the oil, which, if the herb

¹⁾ Report April 1905, 62; October 1906, 58. The places of origin of the oils were Cannes, Cagnes, Castellane, and Barrême.

has been previously dried, are quickly converted by the oxygen of the atmosphere into non-volatile resins, and thus made harmless. As such constituents make the oil entirely useless in certain conditions, it is advisable not to distil the fresh herb, but only the dry, or at any rate the faded, herb. The same applies to many other distilling materials, such as for instance lovage root.

Peppermint Oil, Japanese. So far as the final result of the last harvest can be ascertained, the total output will fall far below the quantity mentioned in our last Report. In London, for instance, it is asserted that at most 2000 cases have been produced, of which one half is said to consist of oil and the other of menthol. Unfortunately no authentic statistics are available on the present occasion.

Business in oil and menthol has been just as unsatisfactory in the course of the last half-year as in the period covered by our last Report, and we scarcely believe that better times are to be hoped for shortly. On the one hand the prices of American oil, which continue to be very depressed, are an obstacle to a revival of the Japanese market, and secondly there continue to be in existence considerable old stocks, both here and in Japan, which also help to weigh upon the market. For many months past those who are interested in the matter in Japan have been vainly endeavouring, by holding the prices firmly, to bring about a renewed interest in it. In spite of all their efforts, consumers only buy for actual requirements. Recently, even a decided slackening of the market has been observed.

Peppermint Oil, Saxon. It would be premature at the present time to express an opinion on the prospects of the coming season's crop, for only when the shoots are beginning to form will it become clear whether the unusually late winter, and particularly the cold weather of the last few months of the past year, which was not accompanied by snow, have or have not exercised an injurious effect upon our cultivations.

Petitgrain Oil, Paraguay. Depressed by the considerable supplies as well as by lower offers for later shipments, the prices again began to move towards a normal level as far back as in the late autumn, and they have now reached a range where the oil promises again to become of interest to consumers. It is, however, more than doubtful whether such low prices as those of former years will return, because it is said that the conditions of manufacture in the country of origin have become very difficult.

Pine-needle Oils. Owing to the weakening of the demand, somewhat large quantities of extra-fine oil from fir cones accumulated, so that it even became possible to effect a slight reduction in

the price. Unfortunately the supplies of the Thuringian distillate, already referred to in our last Report, are very insignificant, for which reason it has not yet been feasible to bring back the price to a normal figure. It is to be hoped that the Thuringian producers will not fail to take advantage of the situation this year, so that it may become possible ere long to leave the Swiss producers, with their exaggerated demands, severely alone. The scarcity of the oil has of course been the signal for a number of firms to endow the international market with all sorts and descriptions of inferior compounds, attracting attention, to be sure, because of their low prices, but wanting both as to the constants and the delicate odour of the genuine oil. Any consumer may prepare such products much more cheaply himself by having recourse to Siberian pine-needle oil. The last-named article is steadily gaining favour among users who are compelled to employ a low-priced oil for the purpose of scenting varnishes, lubricants, dressings, greases, etc. There has been no lack of pine oil from *Abies pectinata* D. C. and *Pinus pumilio* Haenke, and we are justified in asserting that the difficulties which were formerly experienced in procuring these varieties are now probably removed for good.

We avail ourselves of this opportunity to point out that the designation *Oleum Pini silvestris*, which is frequently applied to oil from fir cones (templin oil, *Oleum templini*) is quite a misnomer, and gives rise to constant confusion, for which reason it is desirable that retail-traders as well as others should gradually accustom themselves to accuracy in referring to the oil. We again emphatically lay stress upon the fact that although *Oleum Pini silvestris*, that is to say, oil made from the needles of the common pine (*Pinus silvestris* L.), has often been distilled on experimental scale, yet, owing to its somewhat disagreeable odour, it has never acquired popularity, and has therefore never been manufactured on a large scale. Hence, as we have already stated on a previous occasion¹⁾, it plays no part at all as a commercial article.

The constant confusion of this oil with oil from fir cones (*Abies pectinata* D. C.) has been the cause why genuine oil from pine-needles, notwithstanding that it is unobtainable commercially, has nevertheless been incorporated into Pharmacopœias, for example in the Russian Pharmacopœia and in the Supplement to the 4th Edition of the German Pharmacopœia. At the time when we reviewed these books²⁾ we pointed out that it was quite out of place to make such an oil official, seeing that it was unobtainable. In order to obviate useless correspondence,

¹⁾ Gildemeister and Hoffmann, *The Volatile Oils*, p. 258.

²⁾ Report October 1904, 95; October 1906, 94.

we repeat this statement here, and at the same time we place it on record that the article which goes by the name of *Oleum Pini silvestris* in commerce, is really oil from cones of *Abies pectinata* D. C. (*Oleum templinum*). In the existing conditions it would certainly be better if the designation "*Oleum Pini silvestris*" were to disappear from the commercial vocabulary altogether, and were exclusively reserved to the real oil from pine-needles.

While working up a large parcel of oil from cones of *Abies pectinata* D. C. for l-limonene, we were able to prove definitely the presence of borneol in this oil. Bertram and Walbaum¹⁾, while examining this oil, had already discovered an ester, but they were unable to determine its character, as it only occurs in small proportions in the oil. They surmised that this ester represented bornyl acetate, because this substance is a constituent of almost all pine-needle oils.

The oil worked up by us, and referred to above, possessed the following constants: d_{15° 0,8556, n_{D20° 1,47246, $\alpha_D - 76^\circ 30'$, ester no. 5,3. The oil was freed from terpenes by fractional distillation and saponified. The resultant alcohols were found to boil between 190 and 225°. The principal fraction (b. p. 205 to 215°) was heated with phthalic anhydride and the acid ester formed was recrystallised from alcohol. The m. p. (164°) is that of the acid phthalic ester of borneol. Owing to the smallness of the sample available it was impossible to identify the borneol by other combinations. In addition, there appeared to be present in the oil, another alcohol (b. p. 190 to 197°; d_{15° 0,9013), and a sesquiterpene.

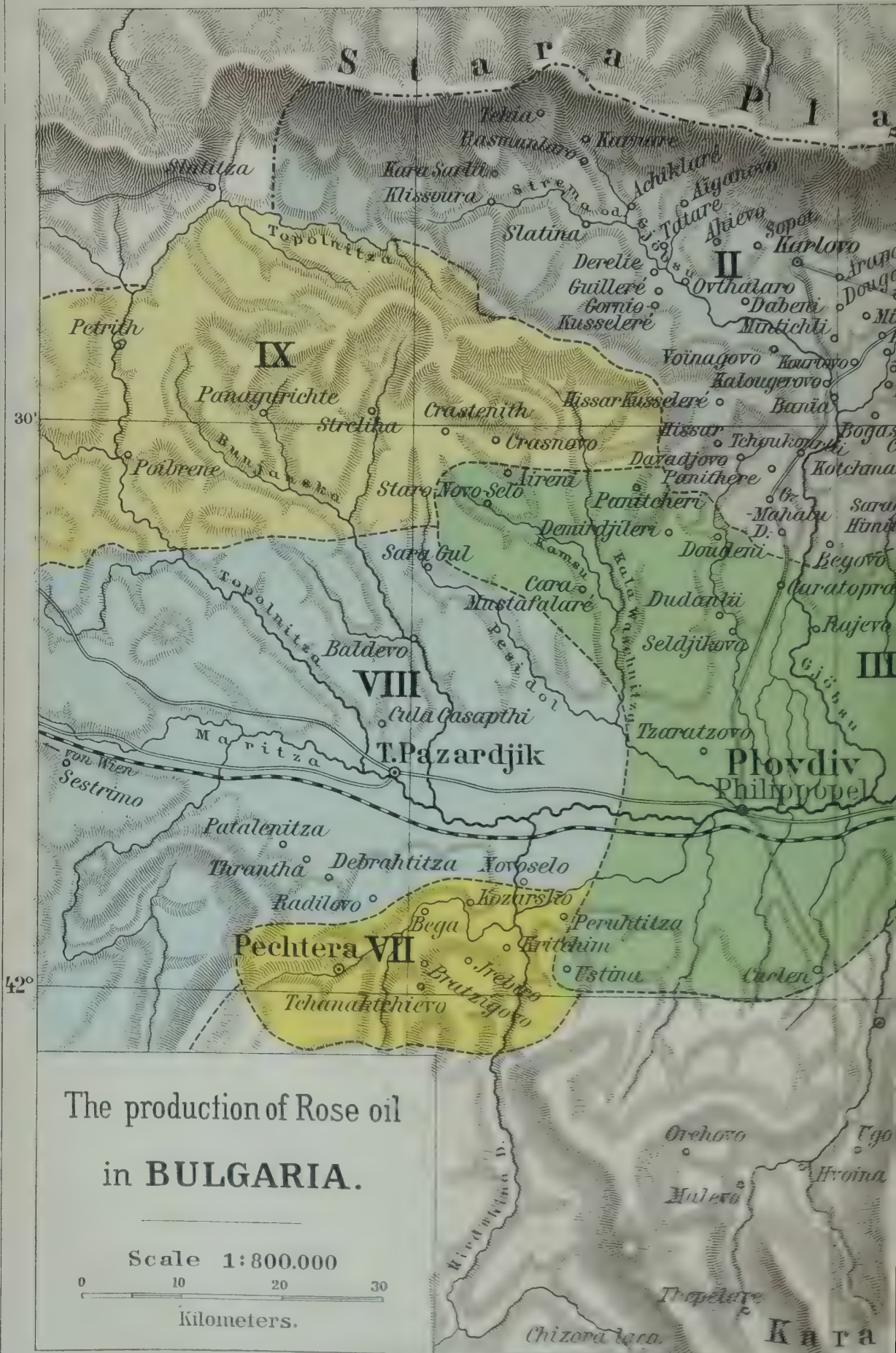
From Siberian pine needle oil, P. G. Golubeff²⁾ obtained by distillation, after heating the oil to 50 to 60° with a mixture of sulphuric and acetic acids and saponifying with alcoholic potash solution, a solid, inactive camphene (m. p. 47 to 48°; b. p. 157 to 158°). When hydrated, this camphene, like the l-camphene obtained from the crude oil of the Siberian pine, yielded i-isoborneol, which was convertible into i-campher (m. p. 178 to 179°, b. p. 204°) by means of nitric acid or permanganate.

From the needles of the Australian pine tree *Callitris glauca* R. T. Baker and H. G. Smith³⁾ obtained 0,6 % of a volatile oil with a content of about 12 to 16 % bornyl acetate and geranyl acetate. The constants of the crude oil moved within the following limits: d 0,8631 to 0,8782, $\alpha_D + 22,7$ to $+ 31,3^\circ$, n_D 1,4747 to 1,4779.

¹⁾ Arch. der Pharm. **231** (1893), 293; Report April 1893, 55.

²⁾ Meeting of the Chem. Section of the Russian phys. chem. Soc., May 8/21, 1908. According to Chem. Ztg. **32** (1908), 922.

³⁾ Roy. Soc. N. S. Wales. Abstract of Proceedings, Aug. 1908, iii. Quoted from Journ. Soc. chem. Industry **27** (1908), 1039.



23°

30'



23°

the following terpenes, viz., d-pinene, d-limonene, and dipentene, were found to occur in the oil. The borneol and its acetate contained in the oil were dextrorotatory.

Upon distilling the wood the authors obtained a thick oil containing guajacol and a new phenol "callitrol".

The sandarach resin yielded by this variety of tree was inferior to that from *Callitris calcarata*.

Rose Oil, Bulgarian. In order to afford a better understanding of the tables relating to the production of rose oil¹⁾ which we published in our last Report, we now present our readers with a map of the districts where rose oil is produced, giving a survey of this interesting region which has been so frequently alluded to in former Reports. In this case also, we are indebted for the data upon which our information is based to Messrs. S. Seraphimoff & Co., of Kazanlik.

Transactions in rose oil have naturally suffered during the past half year under the general depression of trade, and if notwithstanding this prices have remained unchanged, this may be ascribed in the first place to the fact that at the very beginning of the last crop an extremely lively interest for the article was shown on all sides. Any oil which was not sold firm for delivery passed into the hands of wealthy exporters, who were in a position to await the demand without depressing the market with their stocks. It will be clear, without further explanation, that these firms have not experienced much satisfaction from the transactions in rose oil during the past six months, nor experience shows that when business is dull valuable articles are those which excite the least desire to purchase.

Roure-Bertrand Fils²⁾ report on an oil from white Bulgarian roses. It possessed the following constants: $d_{15^\circ} 0,8723$, $D - 2^\circ 54'$, ester no. 11,14, ester no. after acetylation 222,44, corresponding to 74,44 per cent. of alcohols of the formula $C_{10}H_{20}O$. The oil is soluble, with strongly marked separation of paraffin, in a vol. of 90 per cent. alcohol. At $+14^\circ$ it is solid, but at 20° it liquefies completely. Its odour is much less delicate and persistent than that of the oil from red roses, and Roure-Bertrand Fils therefore advise that the latter only should be used for distilling purposes. The fact that the white roses are the less valuable variety is also the reason which, in 1906, induced the Chamber of Commerce of Philippopolis to urge upon the distillers the advisability of abandoning the cultivation of the white roses³⁾.

1) Report November 1908, 105 to 107.

2) Berichte of Roure-Bertrand Fils, October 1908, 28.

3) Comp. Report October 1906, 66.

Rosemary Oil. The prices for French as well as for Dalmatian oil have become decidedly firmer in the course of the last few months, and in the districts of production the supplies are beginning to lessen. On account of the low value, the oil has gained numerous new consumers, especially the French kind, and it is likely that the market may shortly acquire increased firmness.

We have already previously referred to the observations of Birckenstock¹⁾ with regard to the changes, according to the season of the year, in the composition of oil of *Rosmarinus officinalis* L.²⁾

Rue Oil. We have already on a previous occasion referred to an article by Birckenstock³⁾ on the effect of the season upon the oil contained in Algerian rue⁴⁾.

From Corfu we received offers of two oils of sage, which possibly were not derived from *Salvia officinalis* L., because, in contradistinction to ordinary oil of sage, they were lævorotatory. The odour also was different, thujone being less perceptible. The constants of the pale yellow, almost colourless distillates, were as follows: —

$d_{15^{\circ}}$ 0,9153, α_D — $15^{\circ} 14'$, acid no. 0,5, ester no. 9,0
 „ 0,9132, „ — $15^{\circ} 5'$, „ „ 0,5, „ „ 10,6

The oils were soluble in 1,3 vols. of 80 per cent. alcohol and more. Of 70 per cent. alcohol, about 25 vols. were needed to effect solution.

Sage Oil. In a short paper on the present state of research in sage oil, T. F. Harvey⁵⁾ refers to investigations by A. Tompkin, who has examined one Spanish and four Dalmatian oils. The first-named possessed the following constants: d 0,9053, α_D + $9,60^{\circ}$, $n_{D20^{\circ}}$ 1,4619, acid no. 0,6, ester no. 17,2, total borneol 15,2 $\frac{0}{100}$; soluble in 2 vol. of 80 per cent. alcohol. The values of the Dalmatian oils moved within the following limits: d 0,921 to 0,9253, α_D + $9,93^{\circ}$ to + $13,62^{\circ}$, $n_{D20^{\circ}}$ 1,4618 to 1,4645, acid no. 1,3 to 2,2, ester no. 6,7 to 8,5, total borneol 9,5 to 14,8 $\frac{0}{100}$, soluble in 1 and more vol. alcohol. The oils boiled chiefly between 170 and 220° ; below 170° only 2 to 3 $\frac{0}{100}$ passed over, between 170 and 200° 55 to 65 $\frac{0}{100}$, and between 200 and 220° 21 to 31 $\frac{0}{100}$. The corresponding fractions of the Spanish oil were 13,64 and 10 $\frac{0}{100}$. We have made frequent communications about oil of sage in our recent Reports, to which we may here refer⁶⁾.

¹⁾ Journ. de la Parfumerie et Savonnerie **21** (1908), 231.

²⁾ Report October 1906, 69.

³⁾ Journ. de la Parfumerie et Savonnerie **21** (1908), 231.

⁴⁾ Report October 1906, 70.

⁵⁾ Chemist and Druggist **73** (1908), 393.

⁶⁾ Report April 1907, 90; October 1907, 79; April 1908, 89.

Sandalwood Oil, East Indian. About 10 per cent. less wood was placed on sale during the last auctions than in 1907. As was to be expected, little desire for buying was shown, and as, moreover, the Government at first fixed limits which were entirely out of the question, not much more than half of the quantity offered was sold, mostly to private dealers. Further details with regard to the prices as compared with the previous year may be gleaned from the table on page 84.

Altogether about 991 tons remained unsold, and nothing was now for it but to endeavour to obtain limits. This, however, also resulted only partly in business, as the exporters kept themselves very much aloof in consequence of the depressed state of trade in Europe and the United States, and as the offers made ranged very considerably below the ideas of prices entertained by the Government. Finally, however, a few important transactions were concluded at low quotations, and perhaps those concerned in India will learn from the results of the present season the lesson that it is not advisable to ride the high horse too much at the very beginning of the auctions.

The prices of East Indian sandalwood oil remained unchanged last winter, and the end of the continued cutting of prices has been that certain firms have been compelled to vacate the field. In this article only the manufacture on a true wholesale scale, with the most modern and rational appliances — such as are to be found in our works — can be made to pay. In the extension of our factory, which has recently been completed, we have had special regard to the considerable enlargement of our plant for distilling sandalwood, and we are therefore now equipped to meet successfully with all competition.

K. Bode¹⁾ makes a communication on the constituents and properties of East Indian Sandalwood oil. His short paper passes in review our present knowledge of the production, properties and composition of sandalwood oil, and should be of interest to all who wish to make themselves rapidly acquainted with what is best worth knowing about the article.

For the reactions of eksantalal, see Aldehydes, p. 128.

Schinus Oil. In our previous April Report²⁾ we gave some particulars of two schinus oils of Mexican origin. In the meantime we have received another such oil from Mexico, the properties and constants of which are briefly recorded here: pale yellow, $d_{15^\circ} 0,8492$, $d_{20^\circ} + 56^\circ 27'$, $n_{D20^\circ} 1,47616$. Even with absolute alcohol it only at first

¹⁾ Apotheker Ztg. 24 (1909), 17.

²⁾ Report April 1908, 121.

Auction	Fraserpett		Hunsur		Seringapatam		Bangalore		Hassan		Chickmagalur		Tarikere		Shimoga		Sagar		Tirthahalli	
	18./12. 1907	16./11. 1908	16./12. 1907	19./11. 1908	12./12. 1907	23./11. 1908	9./12. 1907	25./11. 1908	5./12. 1907	30./11. 1908	2./12. 1907	3./12. 1908	28./11. 1907	7./12. 1908	25./11. 26./11. 1907	10./12. 1908	21./11. 1907	14./12. 1908	18./11. 1907	17./12. 1908
Prices realised:—																				
2nd Class Billets . .	—	—	—	—	58/3	—	58/6	—	57/6	—	59/6	—	58/-	55/6	—	—	—	—	—	—
3rd „ „ . .	—	—	—	57/-	59/3	55/6	—	—	—	—	59/6	—	59/6	56/-	58/6	—	54/6	—	57/-	—
Ghotla	—	—	—	56/6	—	55/3	—	—	—	—	—	—	—	—	—	—	—	—	57/6	—
Ghatbadala	54/-	55/-	52/-	51/6	52/6	50/5	53/-	—	52/6	49/6	53/3	50/-	54/6	50/6	54/-	—	51/3	—	53/3	49/3
Bagaradad	—	55/-	—	54/-	—	53/3	—	—	54/6	—	—	—	55/6	53/3	55/3	53/-	51/3	—	—	—
1st Class Roots . . .	60/3	60/-	57/-	57/6	—	—	—	—	57/6	56/6	58/6	56/-	59/-	56/6	—	—	56/6	—	58/9	—
2nd „ „ . . .	61/-	60/6	56/9	57/6	—	—	—	—	—	55/-	58/6	55/-	59/-	56/6	—	—	56/3	—	58/6	—
3rd „ „ . . .	—	60/-	—	56/6	—	—	—	—	—	—	—	—	—	—	—	—	—	—	57/3	—
1st „ Jugpokal. .	53/3	54/-	50/-	—	51/3	—	51/3	—	—	47/6	52/3	47/-	52/6	47/-	52/- to 52/9	—	50/3	44/6 to 45/-	50/-	44/6 to 45/-
2nd „ „ . . .	50/6	50/9	—	—	47/3	—	—	—	—	—	48/6	44/-	49/3	—	44/3	48/6	43/-	49/6	—	—
Ain Bagar	—	55/-	—	46/-	47/3	46/-	—	—	47/9	—	47/6	—	—	—	47/6	—	—	—	46/6	—
Cheria.	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	44/3	—
Ain Chilta	—	—	33/3 to 34/9	33/3	33/-	—	32/9	—	33/6	32/6	33/3	32/9	33/3	33/-	32/3	—	32/-	—	32/3	—
Hatri Chilta.	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Milwa Chilta	22/6	—	22/9	20/6	22/6	19/9	23/-	—	23/-	20/6	22/6	19/9	23/6	19/9	22/9	—	23/3	19/-	22/6	19/-
Basola Bukni	—	17/-	16/3	—	16/3	—	16/3	—	16/9	—	—	15/6	—	14/6	19/-	—	19/-	—	19/-	14/6

gives a clear solution; when more than 0,7 vol. of alcohol are added, cloudiness ensues. The oil is very rich in phellandrene. Unfortunately we have not heard whether the oil is prepared from the leaves or from the fruit; the distillates from both these parts (as has been pointed out in previous Reports) being almost identical.

Snake root Oil, Canadian. Two Canadian snake root oils distilled by ourselves from *Asarum canadense* L. possessed the following constants: —

No. 1. From roots with fibres: $d_{15^{\circ}}$ 0,9519, α_D — $10^{\circ}30'$, $n_{D20^{\circ}}$ 1,49987, acid. no. 4,7, ester no. 74,7, ester no. after acetylation 125,0, soluble in 2,5 vols. and more of 70 per cent. alcohol.

No. 2. From roots without fibres: $d_{15^{\circ}}$ 0,9520, α_D — $10^{\circ}42'$, $n_{D20^{\circ}}$ 1,48863, acid no. 3,1, ester no. 86,1, ester no. after acetyl. 125,8, soluble in 2,3 vols. and more of 70 per cent. alcohol.

Spearmint Oil. The excitement which prevailed in this article last summer has completely subsided, and prices move within normal limits. A large part of last year's crop had been contracted for in advance, and has been used up in the manufacture of chewing-gum. Enough was left, however, to cover the remaining requirements and there are signs that during the current year also a sufficiency of oil will be available at reasonable rates. But little spearmint is nowadays cultivated in the State of New York, which is to be regretted, because the oil yielded by the New York herb was superior in quality to the oil from Michigan.

We have recently had several opportunities of examining Hungarian spearmint oils. We were informed that they had been distilled from the dry herb. Their composition is similar to that of the German and American distillates, but they differ from them in their higher carvone content, which runs up to 72% as against only about 50% in German and American oils. Corresponding with their greater carvone content the specific gravity of the Hungarian oils was also in every case higher than that of the other varieties, and their greater solubility also attracted attention. The Hungarian oils give a clear solution with 1 vol. and more of 80 per cent. alcohol, whereas German and American oils, although likewise soluble in equal volumes of 80 per cent. alcohol, give an opalescent solution, and subsequently a turbid one when more of the solvent is added. The following are the constants noted in Hungarian oils: $d_{15^{\circ}}$ 0,936 to 0,944, α_D — $38^{\circ}38'$ to — $46^{\circ}25'$, $n_{D20^{\circ}}$ 1,490 to 1,491, carvone content 61 to 72%. All the samples gave clear solutions with their own vol. and more of 80 per cent. alcohol; one sample even dissolved clearly in 2,5 vols. and more of 70 per cent. alcohol.

In order to make sure that no carvone from caraway oil had been added to the samples, the carvone was in each case separated out with neutral sodium sulphite and regenerated. The specific gravity was about 0,965 (15°); the rotation lay between $-58^{\circ} 7'$ and $-59^{\circ} 50'$. From the normal character of the rotatory power it is evident that no dextrorotatory carvone from caraway oil was present.

Spike Oil. Under the weight of the commercial depression the prices receded further in the course of the winter, until at last the position induced a few large buyers to cover their requirements. At the present time the stocks in first hand have become greatly reduced, so that the quotations for pure quality have risen from about fr. 5 to fr. 6.50, while in some districts holders are already asking fr. 7. As a result of our holding large stocks, we are for the present able to maintain our prices, but if the upward movement should become more pronounced we shall soon be compelled to follow it.

Birckenstock's¹⁾ observations with regard to the differences which exist between spike oils derived from plants of different origin have already been discussed by us on a previous occasion²⁾.

Spruce Oil. This oil is used in considerable quantities in the United States, principally for liniments and veterinary medicines. It has been distilled in the mountains of Massachusetts, Vermont, and New Hampshire for the past one hundred years or more. This work is done by farmers who have a still in some suitable place on their farms and when other farm work is not pressing, distil oil. This, however, they do only in summer, as none of them put money enough into their outfits so that they could run them in winter.

For distillation the small trees are cut which grow in the pastures and from them the smallest branches are trimmed. The stills consist of wooden tubs and iron worms and generally do not last more than two or three years. Several years ago oil was so low and farm labour so high that the farmers did not renew their stills when they became defective, and failed to work. At that time also some dealers began to buy up spruce brush to be shipped to the cities for use in cemeteries, and \$ 4.00 was paid per ton, from which quantity about 15 lbs. of oil can only be obtained.

In 1906 spruce oil was very scarce and prices went up to 65 cts. per lb. Since that time a large number of farmers have put in new stills and oil was run as fast as possible. The farmers offered their oil freely to dealers and wholesale druggists, which caused a heavy decline in price,

¹⁾ Journ. de la Parfumerie et Savonnerie **21** (1908), 234.

²⁾ Report October **1906**, 73.

the consequence of which will be that no new stills will be put up from now on and that the old stills will not be renewed when out of working order.

Prices may soon advance again. The paper pulp industry is consuming large quantities of trees and as it is reckoned that growing spruce pays ten per cent. interest on its value simply by growing, it can be readily seen why the owners of spruce land hesitate making the trees into oil, unless at a very high figure.

Star anise Oil. Even the price of 4/-, which was reported in November last, did not mark the lowest point touched by the article, for in the month of December a somewhat considerable transaction was actually concluded at $3/11\frac{3}{4}$. Since then, the quotations have moved between 4/- and 4/2, but within the last few days an easier tendency has again manifested itself, and for the present has dashed all hopes of an upward course of the value. Tonquin star anise oil has also been available in plenty last year, but the considerable business which took place was not always concluded without claims, as on several occasions cases filled with stones were found among the consignments. The proceedings which in some instances have been instituted against the shippers of these goods by the insurance companies will, it is hoped, clear up the question whether robbery had been committed during the voyage, or whether irregularities had taken place in the course of shipment at the other side.

Oil of *Tagetes patula*. In our Report of November 1908, p. 141, we gave some particulars of the oil of *Tagetes patula* L. obtained from the fresh umbels with the involucre. We are now in a position to add the following details.

We made the umbels (all of which were of the same crop) air-dry, and then subjected them to steam distillation. The yield of oil was 0,08 % from the fresh, and 0,57 % from the dried umbels and was of a brownish yellow colour; it scarcely differed from the oil previously described. Its constants were as follows: $d_{15^{\circ}}$ 0,8925, $d_D - 9^{\circ}$, $n_{D20^{\circ}}$ 1,49938, acid no. 6,4, ester no. 10,6, soluble in 9 to 10 vols. of 90 per cent. alcohol, producing cloudiness; miscible with 95 per cent. alcohol.

The oil obtained from the air-dried stalks and leaves by water- and steam-distillation showed similar properties. Of this oil we obtained 0,07 % from the fresh, and 0,218 % from the dried herb. $d_{15^{\circ}}$ 0,9034; $d_D + 1^{\circ} 15'$; $n_{D20^{\circ}}$ 1,49938; acid no. 14; ester no. 12,4 (after heating again the ester no. was 10,6); not clearly soluble in 10 vols. of 90 per cent. alcohol; miscible with 95 per cent. alcohol. From the saponification-liquors, a fatty acid (palmitic acid) m. p. 62° , could be separated after repeated re-crystallisation.

Tansy Oil. Good American oil continues to remain very scarce, and the small supplies which we have obtained through the intermediary of our New York branch, have quickly found buyers at full prices.

Tetranthera Oils. The Buitenzorg Annual Report for 1907¹⁾, contains brief references to tetranthera oils which, like those examined by Charabot and Laloue and mentioned in our Report of April last²⁾, were produced in the Malay Archipelago, in the Island of Java. The Buitenzorg examinations related to three distillates, one each from the bark, the leaves and the fruit respectively, and resulted as follows:—

1. Oil from bark. Yield about 0,13%, $d_{26^{\circ}}$ 0,856, $\alpha_D + 20^{\circ} 24'$, contained 78,5% aldehydes.

2. Oil from leaves. $d_{26^{\circ}}$ 0,890, $\alpha_D - 12^{\circ} 12'$, contained much cineol and 22% aldehydes.

3. Oil from fruits. Yield about 3,9%, $d_{26^{\circ}}$ 0,876, $\alpha_D + 12^{\circ} 44'$, on fractional distillation, 19% passed over up to 200° , 61% between 200 and 220° , and 14% between 220 and 240° . The oil contained 85% aldehydes, of which 64% was citral.

In connection with the above we may here refer to our own results, obtained with tetranthera oils from the same source:—

An oil from bark possessed the following characteristics: $d_{15^{\circ}}$ 0,9062, $\alpha_D + 13^{\circ} 58'$, $n_{D20^{\circ}}$ 1,46595, ester no. after acetylation 230,2, soluble in 1 vol. and more of 80 per cent. alcohol. This oil was of a pale-yellow colour; its odour reminded of Java citronella oil, and it obviously contained much citronellal, 76,5%, judging from the acetylation number.

An oil from leaves was also pale-yellow and had a pronounced cineol-odour. It contained, in fact, about 35% of this body, obtained with resorcinol in the form of a solid compound. Other components parts were citral (6% determined with neutral sulphite) and probably also citronellal. The constants were as follows: $d_{15^{\circ}}$ 0,8990, $\alpha_D - 12^{\circ} 2'$, $n_{D20^{\circ}}$ 1,46426, soluble in 1 vol. and more of 80 per cent. alcohol. The diluted solution opalesces.

Two oils distilled from fruits were of a lemon-yellow colour and possessed an odour somewhat like that of lemongrass oil, which is accounted for by the fact that their principal constituent was citral. As the aldehyde determinations with bisulphite gave higher figures than did those with neutral sulphite, it follows that in addition to citral other aldehydes (citronellal, fatty aldehydes) which do not react with neutral sulphite, must be present.

¹⁾ Jaarboek van het Departement van Landbouw in Nederlandsch-Indië 1907, 67. Batavia 1908.

²⁾ Report April 1908, 100.

a) $d_{15}^{\circ} 0,8932$, $\alpha_D + 6^{\circ} 8'$, $n_{D20}^{\circ} 1,48141$, soluble in 2,3 vol. and more of 70 per cent. alcohol, aldehyde content determined with bisulphite about 85%, with neutral sulphite about 75%.

b) $d_{15}^{\circ} 0,8849$, $\alpha_D + 11^{\circ} 30'$, soluble in 3 vol. and more of 70 per cent. alcohol, from 5 vol. and upwards increasing opalescence. Aldehyde content 79% (bisulphite) or 74% (neutral sulphite).

Oil from *Thuja plicata* (Red Cedar). In our recent Reports¹⁾ we have dealt with the investigations made by Blasdale and by Brandel and Dewey respectively on the oil prepared from the leaves of *Thuja plicata* (red cedar), a native of North America. We have recently distilled a similar oil ourselves from the air-dried leaves of trees which had been planted in the South of France, Prof. Heckel, of Marseilles, having very kindly procured for us the material for distillation. The oil, which was obtained to the extent of 1,32%, was of a pale yellow colour and possessed a strong odour of thujone: $d_{15}^{\circ} 0,9056$, $\alpha_D + 5^{\circ} 4'$, $n_{D20}^{\circ} 1,45721$, acid no. 0,8, ester no. 16,9, soluble in 70 per cent. alcohol with opalescence only (about 1:8) but giving a clear solution in 1,2 vols. and more of 80 per cent. alcohol. The thujone separated from the oil with the aid of semicarbazide proved to be identical with α -thujone; the semicarbazone melted at 185 to 186° after being twice re-crystallised from alcohol, and the thujone regenerated from it with phthalic anhydride had a rotation of $\alpha_D - 5^{\circ} 12'$.

We desire to call special attention to the fact that Blasdale's oil and our's were dextrorotatory, while Brandel and Dewey describe their oil to be lævorotatory.

The botanical names in use for the American tree may also be of interest, and are therefore set forth below: *Thuja plicata* Lamb. non Don., *Th. gigantea* Nutt., *Th. Menziesii* Dougl., *Th. Douglasii* Nutt. and *Th. Lobii* hort. (or rather *Th. Lobbi* hort.; the name being derived from Lobb, who introduced the tree into Europe from Western North America in 1853).

Turpentine Oil. An announcement on the part of the Government of Algeria²⁾, to the effect that the Forestry Authorities intend, in the course of the month of March, to sell by auction ten "*Coupes de régénération*" covered with Aleppo pines and occupying a total area of about 550 hectares, situated in the districts of Télagh and Bel-Abbès, appears to show that the manufacture of turpentine distillates is receiving attention in other regions than those in which the production of turpentine oil is being carried on at present. In the case of six of these timber-felling plots it will be allowed to tap the trees

¹⁾ Report October 1907, 91; November 1908, 117.

²⁾ Bull. de l'Office du Gouvern. Gén. de l'Algérie 15 (1909), 50.

four years in succession until they are exhausted (“à mort”) and to cut them down to the stump in the fifth. It is estimated that these plots will yield about 6500 cubic metres of timber and about 400 hectolitres of resin. The trees in the other four plots, estimated at about 30000, may only be tapped for four years without killing (“à vie”). A small plan of the site which accompanies the announcement shows the position of the separate plots and the distance of each from the main lines of traffic.

According to R. Adan¹⁾, when examining oil of turpentine for the presence of mineral oil, the old Burton's test is to be preferred to Herzfeld's process²⁾, because the formation of a residue insoluble even in fuming sulphuric acid does not suffice to prove the presence of benzine, inasmuch as the said residue may also owe its existence to the presence of resin spirits. The best way of carrying out Burton's test is by pouring, drop by drop, 100 cc. of the oil into 300 cc. of fuming nitric acid, and by weighing or measuring the insoluble residue (which should not exceed 2%), after washing it out with hot water. Pure resin spirits (d_{15° 0,8656, n_{D15° 1,4826), when treated with nitric acid, yielded only 2,1% of residue (n_{D15° 1,455); but when treated with sulphuric acid they yielded as much as 17% (d_{15° 0,8472, n_{D15° 1,463). Fractional distillation of the resin spirits resulted as follows: 8% of a b. p. from 118 to 150°, 51% of b. p. 150 to 180°, 27% of b. p. from 180 to 220°, 10% of b. p. 220 to 295°; residue 4%. Burton's test is therefore also well suitable for detecting the presence of benzine in resin spirits. If, in addition, the parts which boil over between 120 and 150° are miscible with aniline and acetic anhydride, the absence of benzine is established.

Wintergreen Oil. Owing to a plentiful output and a somewhat diminished sale, the prices have slowly receded, and a sufficiency of oil of sweet birch of reliable quality is available. The production has again increased, both in Pennsylvania and in the more Southern States. The present low price should be an inducement to lay in a sufficient supply, as it is known that during the summer the producers are otherwise occupied, while the increasing consumption tends to put up the prices.

Oil of Wintergreen leaves. The demand for genuine oil of Gaultheria existing exclusively in the United States has been rather less than in the preceding year and we have therefore been able to supply all the requirements of our customers.

¹⁾ Bull. Soc. Chim. Belgique 22 (1908), 389. Quoted from Chem. Zentralbl 1908, II. 1749.

²⁾ Report April 1904, 85 and 86.

As we have repeatedly stated, our New York branch disposes of the output of several suppliers of established repute, whose names we are of course precluded from publishing on account of business considerations.

Although the majority of our suppliers are personally known to us, every delivery which reaches us is subjected to the most severe chemical examination, and we are in a position fully to differentiate between synthetic oil, sweet birch oil, and oil of wintergreen leaves. Quite recently, parties in Carolina and in New England have taken up the distillation of *Gaultheria procumbens*, and we are expecting sample-consignments of this oil.

H. D. Gibbs¹⁾ reports on the separation of salicylic acid and methyl salicylate, as well as on saponification-experiments made with the ester, problems occurring in the examination of pharmaceutical preparations or of lemonades and other non-alcoholic beverages. The two compounds above mentioned often occur together and it is possible (apart from deliberate addition) that the presence of the acid or its salts may be due to the existence, as an impurity, of free acid in the synthetic ester, wintergreen oil, or sweet birch oil which has been used, or that a splitting-up has occurred. The free acid can be titrated directly. In order to separate it from the ester it is first extracted by frequent shaking with a solution of bicarbonate of sodium of known strength; from this, the ester is removed with chloroform, after which it is acidulated with sulphuric acid 1:3, shaken out with chloroform and determined by titration or by the colorimetric process. By this method, samples of synthetic ester were found to contain 0,0113%, such of wintergreen oil 0,025 to 0,028% of free acid. In the examination of cod liver oil emulsions the bicarbonate-layer was removed by centrifugal action. The ester extracted by chloroform was saponified by boiling it for half an hour with solution of caustic alkali, after which the chloroform was driven off, the sample under examination filled up to a known volume in an aliquot part of the solution and the salicylic acid content determined. Experiments on the rate of saponification of the ester by means of carbonate and bicarbonate of sodium (by shaking solutions of known strength with an excess of ester at 30°), showed that when sodium carbonate was used equilibrium was reached in about a month's time, when the whole of the carbonate had been converted into bicarbonate, whereas in the case of bicarbonate no perceptible saponification was to be observed. When caustic soda solution was employed the saponification was completed in about 24 hours.

¹⁾ Journ. Americ. chem. Soc. **30** (1908), 1465. Philippine Journ. of Science **3** (1908), A. 101.

Furthermore, Gibbs¹⁾ determined the solubility of methyl salicylate in water and in $\frac{1}{10}$ normal sulphuric acid at 30° C. The former solubility was found to be on the average 0,074 g, the latter 0,077 g, each for 100 cc. solvent.

We can only briefly mention here an article by G. R. Pancoast and W. A. Pearson²⁾ on methods for distinguishing between natural and artificial methyl salicylate. We abstain from a detailed description of the process, because the methods indicated are hardly likely to effect their object in a manner which is at all desirable for practical purposes.

Wormwood Oil. The scarcity of French oil, which has arisen from causes which we have already explained, has become more and more pronounced, and as our supplies grew less we were compelled to raise the prices in proportion. It will probably be necessary shortly to look forward to the entire disappearance of this article from commerce. American oil also remains very scarce and dear, and has again advanced in price, which is not surprising, seeing that the demand for this variety has naturally become greater lately.

To the statements made in our Report April 1908, 119, on the projected prohibition of absinthe throughout the Swiss Confederacy, we are now able to add the information that as the result of the *Referendum* of 5th July 1908, the Swiss People have passed a resolution prohibiting, as from October 7th 1908, the manufacture, importation, transport, sale, and storage for the purposes of sale, throughout Switzerland, of the liqueur known as "absinthe".

The prohibition also applies to all beverages, by whatever other name they may be called, which are imitations of this liqueur. Only the transit trade and the use for medicinal purposes are still permitted. The Act comes into force two years after the date of its passing, that is to say, on October 7th, 1910. The executive of the Confederacy is empowered to issue similar prohibitions in respect of all other beverages containing absinthe which constitute a public danger.³⁾

L. Duparc and A. Monnier⁴⁾ have modified Legal's test (recommended by Rocques⁵⁾ for the determination of thujone in liqueurs, and they claim that their method obviates a confusion of thujone with other compounds, including citral. The process is as follows:

¹⁾ Philippine Journ. of Sc. 3 (1908), A. 357.

²⁾ Americ. Journ. Pharm. 80 (1908), 407.

³⁾ Chemische Industrie 32 (1909), 134.

⁴⁾ Ann. chim. analyt. appl. 13 (1908), 378. Quoted from a copy kindly sent to us.

⁵⁾ Comp. Report November 1908, 127.

o cc. of a solution in 60 % alcohol of the sample under examination are first treated with 2 cc. zinc sulphate solution (1:10) and afterwards with 0,5 cc. of a solution of sodium nitro-prusside (1:10). After shaking, 4 cc. of 5 % sodium solution, free from carbonic acid, are added, and one minute later 2 to 3 cc. of glacial acetic acid. The currant-coloured precipitate formed is claimed to indicate the presence of thujone even in dilutions up to 1:5000. It settles in the course of a few minutes. If a garnet-red coloration should ensue upon the addition of the acetic acid it can be removed by shaking with ether. In the case of all other bodies which have been investigated, citral excepted, the precipitate is of a paler colour. Any citral which may be present should therefore be removed in advance by prolonged boiling with aniline phosphate.

In connection with the above reference may be made to a work by L. Duparc on liqueurs seized, designated as imitations of absinthe. This work, which has been published as a pamphlet¹⁾, deals with the manufacture of absinthe, the composition and especially the toxic character of the essential oils used, and their emulsifying properly. It also contains detailed references as to the definition of absinthe and the various methods employed for its analysis.

Ylang Ylang Oil. The sale of this oil, which is so important an article in the perfume industry, has suffered severely during the past half year from the general depression, although the suddenly acquired popularity of Lily-of-the-valley scents opened up a new and favourable prospect, especially for our recognised first-class quality. Even in spite of the excellent artificial Lily-of-the-valley scents which are now available, the use of ylang ylang oil cannot be dispensed with in the preparation of high-class perfumery of this kind.

In our last report we referred briefly to the exports of ylang ylang oil from Réunion. Complete statistics are now available as to the shipments of this oil from the island for the whole of the year 1908. These show that in the period named 1126 kilos were exported, compared with 523 kilos in 1907. The production has therefore more than doubled. The samples of Réunion oil which we have had an opportunity of examining, although showing normal characteristics, cannot compare in odour with first-class Manila quality.

According to a report issued by the Bureau of Insular Affairs²⁾ the sale of ylang ylang oil in the Philippines in the fiscal year 1908 reached the exceptionally high value of \$ 181638.

¹⁾ L. Duparc, Rapport d'expertise sur les liqueurs saisies qualifiées d'imitations de l'absinthe. Geneva, 1908.

²⁾ Nachrichten für Handel und Industrie 1909, Nr. 4, p. 2.

Roure-Bertrand Fils¹⁾ have ascertained the following values in an ylang ylang oil from Réunion. The figures agree with those of Manila oil: d_{15° 0,9492, α_D — $30^\circ 8'$. Ester content (calculated as linalyl acetate) 33,6%, total alcohol (calculated as linalool) 40,3%. Soluble in 0,5 to 1 vol. of 90% alcohol, followed shortly afterwards by slight cloudiness.

A Réunion oil examined by us years ago²⁾ showed the high specific gravity of 0,974 (15°).

In an article by M. Mücke³⁾ on the plant yielding ylang ylang oil, and the production of the latter, we find *inter alia* a few details concerning cultivation experiments at Amani which have been carried out by the German Biologico-Agricultural Institute. According to these experiments, the ylang ylang tree appears in the said district not to thrive very well at altitudes of 900 m.; but it does well at up to 450 m. altitude. Mücke assumes that the limit of altitude of the ylang ylang tree lies between 500 and 550 m. This assumption appears to correspond with the statement by Flacourt⁴⁾ relating to Réunion, which has a more southerly position and where the limit of altitude of the tree is about 400 m.

New essential oils.

Oil from *Barosma pulchellum*. In addition to the varieties of *Barosma* which are of interest in the preparation of buchu leaf oil, i. e. *Barosma betulinum* (Thunb.) Bartl. et Wendl., *B. crenulatum* (L.) Hook., and *B. serratifolium* (Curt.) Willd., the leaves of other species have lately been met with in the London market on several occasions. Some years ago, Sage⁵⁾ reported on leaves of *Diosma succulentum* var. *Bergianum*, known as Karoo Buchu, which are reputed to yield an oil equalling that of *Barosma betulinum* in value. In other quarters, however, leaves have also been noticed of which the oil, by its mere odour, betrays a composition differing materially from that of the ordinary buchu leaf oil. The leaves of *Barosma pulchellum* (L.) Bartl. et Wendl., as well as those probably derived from *Agathosma variabile* (Lond.) belong to the latter category. The last-named leaves have also been described by Sage⁶⁾ who, on account of their anise-like

¹⁾ Berichte of Roure-Bertand Fils, October 1908, 29.

²⁾ Gildemeister and Hoffmann, *The Volatile Oils*, p. 364.

³⁾ Der Pflanze 4 (1908) 257.

⁴⁾ Comp. Report April 1904, 89.

⁵⁾ Chemist and Druggist 65 (1904), 506, 717. Report April 1905, 12.

⁶⁾ Pharmaceutical Journal 80 (1908), 125.

odour, called them "Aniseed Buchu". These leaves are ovate-lanceolate, leathery, 5 to 8 mm. long and 3 mm. wide and bear a resemblance to Karoo Buchu. Sage intends to make further investigations with the object of discovering whether the botanical designation aforementioned is correct.

E. M. Holmes¹⁾ was the first to call attention to the occurrence of leaves from *Barosma pulchellum*. They differ from the *betulinum* leaves by their citronella-like odour as well as by being smaller. Their length runs from 7 to 12 mm., their width is 4 mm. They have very short stalks, are ovate to ovate-lanceolate, serrulate, obtuse, and broadest at the base of the leaf. Like the other varieties of *Barosma*, the shrub is a native of Cape Colony. In order to enquire further into the question whether the oil would eventually possess a commercial value, we obtained from London a considerable parcel of the leaves. Dr. Giessler, "Custos" at the Botanical Institute of Leipzig University, who has examined the material as regards its botanical origin, has ascertained that it really represented *Barosma pulchellum* (L.) Bartl. et Wendl. Leaves of the closely related *B. pulchellum* var. *majus* and *B. latifolium* (L. f.) Röm. et Schult. also occurred in the parcel.

Upon distillation the leaves yielded 3 0/0 of a golden-yellow oil, with an odour reminding chiefly of citronella, but possessing at the same time an unpleasant narcotic subsidiary odour, which constitutes a direct objection to the use of the oil. The specific gravity was 0,8830 (15°), opt. rot. $\alpha_D +8^\circ 36'$, n_{D20° 1,45771, acid no. 18,5, ester no. 27,2, ester no. after acetylation 237,0 = 79,3 0/0 $C_{10}H_{18}O$. We are able to give the following details with regard to the examination of the oil, which is however not yet concluded: —

The disagreeable subsidiary odour referred to above is due to a base. This was abstracted from the oil (which was kept cool) by treatment with 25 0/0 tartaric acid solution. The base, separated from the tartaric acid solution by means of carbonate of soda, possessed an extraordinarily penetrating narcotic odour. It had a rather inconstant b. p. between 130 and 140° (5 mm. press.). (The quantity of the material employed was barely 1 g.) From the hydrochloric acid solution, on treatment with platinum chloride, no crystals separated off.

The citronella-like odour of the oil freed from the base made us suspect the presence of citronellal. As a matter of fact the oil reacted with bisulphite liquor partly neutralised by sodium carbonate, a crystalline mass being separated. From the latter, after filtering with the suction pump and purifying with alcohol and ether, an aldehyde was liberated by warming with carbonate of soda solution. Its constants showed it to be citronellal;

¹⁾ Pharmaceutical Journal 79 (1907), 598; compare also Chemist and Druggist 71 (1907), 702.

b. p. 73 to 75° (7 to 8 mm. press.), b. p. 205 to 208° (atmosph. press.), $d_{15} 0,8560$, $\alpha_D + 13^{\circ}6'$, $n_{D20} 1,44710$. Its semicarbazone melted at 81 to 82°. From 500 g. of oil we isolated about 220 g. of aldehyde. The smaller part of the oil freed from citronellal passed over between 45 and 103° (5 mm. press.), the larger portion remained behind in the flask in the form of a brown, viscous oil. The fractions with the lowest b. p. contained small quantities of methylheptenone, which was separated in the form of a semicarbazone. Only after recrystallising it three or four times from dilute alcohol the m. p. of this derivative was found to be 134 to 135°. This circumstance, as well as the fact that when the odour observed was not that characteristic of methylheptenone, but rather reminded of a saturated fatty ketone, indicated the presence of another, additional, ketone. The semicarbazone referred to above, when mixed with that from the pure methylheptenone, showed no depression of the melting point.

In a fraction having the b. p. 75 to 82° (5 mm. press.) and the opt. rot. $+ 6^{\circ}54'$, small quantities of d-menthone could be detected, but only through the semicarbazone. Only when the oil mixed with it had been removed from the semicarbazone solution by steam distillation, the derivative could be obtained in the solid form. After repeated recrystallisation from alcohol it melted at 178 to 181° and when warmed with diluted acid it developed the unmistakable odour of menthone. Efforts were also made, unfortunately without success, to separate by means of the oxime larger quantities of menthone from the fractions which preceded and succeeded the one referred to above, and to reconstitute the ketone from them. It is therefore probable that the somewhat pronounced odour of mint which attached to all these fractions is ascribable to the presence of isopulegol. This isopulegol obviously owed its existence to the action of acids upon the citronellal.

Further, in the portions of the oil boiling between 75 and 103° (5 mm. press.) we discovered an alcohol of a rose-like odour, which was ascertained to be d-citronellol. For the purpose of identification the fractions were treated in the well-known manner with phthalic anhydride. The citronellol separated by saponification from the solution of the sodium salt of the acid phthalic ester and distilled over with water vapour, possessed the following constants: b. p. 93 to 95° (5 to 6 mm. press.), $d_{15} 0,8732$, $\alpha_D + 2^{\circ}14'$, $n_{D20} 1,46288$. The silver salt prepared from the free acid phthalate, after being recrystallised from benzene and methyl alcohol, showed the characteristic melting point for this salt (125°) and the theoretically required silver content: —

0,2774 g. subst.: 0,0727 g. Ag.

Found:
Ag 26,21 %

Calc. for $C_{18}H_{21}AgO_4$:
26,23 %

When the original oil was treated with highly-diluted soda liquor it proved to contain an oily acid of a high b. p. as well as traces of a phenol. In order to separate these two the oil, after being recovered from the soda liquor, was treated with carbonate of soda solution. The acid which had separated from the carbonate solution on acidulation may, however, not be a uniform one, as might be concluded from its b.p. and its behaviour as detailed below. Apart from an unimportant first runnings (b. p. 115 to 125°, 5—6 mm. press.) it boiled at 125 to 131°. Its other constants were as follows: b.p. 257 to 263° at normal press., d_{15}° 0,9394, $a_D + 5^{\circ} 2'$, n_{D20}° 1,45611. These properties, and the silver content as ascertained by analysis of its silver salt recrystallised from water, indicate citronellic acid $C_{10}H_{18}O_2$: —

0,3079 subst.: 0,1196 g. Ag.

Found:	Calc. for $C_{10}H_{17}AgO_2$:
Ag 38,84 %	38,77 %

In order to identify the acid more closely recourse was had to the amide of citronellic acid, m. p. 81 to 82°. For its preparation, the acid was first converted into the chloride (b. p. 122 to 125°, 6 mm.) by means of thionyl chloride, and the latter converted into the amide with aqueous ammonia. The amide purified from petroleum ether melted not quite sharply at 87 to 88°, that is to say, 6° higher than that obtained by Tiemann¹⁾ from citronellic acid nitrile. It is our intention, for purposes of comparison, to prepare the amide of synthetic citronellic acid, in order to determine by this means whether the above-mentioned acid really represents citronellic acid (the existence of which in essential oils has not been detected up to the present), or another acid of the same constitution. In addition to the arguments adduced above, its identity with citronellic acid seems to be indicated by the fact that the oil contains both citronellol and citronellal.

Only traces of the phenol referred to above were at our disposal. These were just sufficient to enable us to identify it by its benzoyl combination. This body, obtained by Schotten-Baumann's method, when purified from petroleum ether, had a m. p. of 109 to 110°, but up to the present we have been unable to identify it with the benzoate of any known phenol.

From the Instituto Médico Nacional in Mexico we received the two following distillates: —

Oil of Satureja macrostema (Benth.) Briq. (*Calamintha macrostema* Benth.). The oil of this shrub-like plant, which belongs to

¹⁾ Berl. Berichte 31 (1898), 2899.

the N. O. *Labiatae* and is a native of Mexico, was pale yellow and had an odour resembling that of mint; $d_{15^{\circ}}$ 0,9182, $\alpha_D + 6^{\circ} 51'$, $n_{D20^{\circ}}$ 1,46852, acid no. 15,6, ester no. 10,3, ester no. after acetylation 37,9. The oil is soluble in any proportion of 90 per cent. alcohol, also in 3 vols. of 70 per cent. or 1,2 vol. of 80 per cent. alcohol, but opalescence ensues with the last two when more of the solvent is added. The odour points to the presence of pulegone.

Oil from the Mexican Marsh-cypress (*Taxodium mexicanum* Carr., *T. Montezumae* Decne., *T. mucronatum* Ten.). This tree, which belongs to the conifers and is known in Mexico as "Sabino", grows in that country at altitudes of from 5600 to 7000 ft. It is not distributed over a very wide area, but where it does grow it forms large forests.¹⁾ The oil, which had probably been distilled from the leaves, was of a pale brown colour and somewhat resembled, in its odour, oil of turpentine, to which it is probably also closely allied in its composition. $d_{15^{\circ}}$ 0,8685, $\alpha_D - 10^{\circ} 20'$, $n_{D20^{\circ}}$ 1,46931, acid no. 0,5, ester no. 5,7; soluble in 5,4 vols. and more of 90 per cent. alcohol.

Oil of Artemisia Herba-alba var. densiflora Bois (Chieh Oil). From Egypt we received, for the purpose of examining it for essential oil, a herb which is known there by the name of "Chieh", and which occurs on the high limestone plateaus of Egypt and Tripoli and probably also in Arabia. The plant is said to reach its full development early in March and to flourish particularly in rainy years. The Arabs and Tuaregs employ a decoction of the herb medicinally as an emollient and diuretic. Owing to the sample sent to us being imperfect, great difficulty was experienced in determining its botanical name. Prof. Heckel, of Marseilles, who kindly examined the sample for us, and to whom we owe thanks for his courteous assistance, informed us under reserve that the herb was probably an *Artemisia Herba-alba*. This opinion was confirmed on further investigation when a few specimens which had been carefully pressed between paper were sent to us. Dr. Giessler, "Custos" at the Botanical Institute of the University of Leipzig, was able to ascertain that the sample represented a variety of the above-mentioned plant, viz., *A. Herba-alba* var. *densiflora* Bois.

By water vapour we obtained from it a yield of 1,6% of a yellowish oil, with a clear odour of thujone, which upon examination gave the following results: $d_{15^{\circ}}$ 0,9192, $\alpha_D - 5^{\circ} 20'$, $n_{D20^{\circ}}$ 1,45611, acid. no. 1,5, ester no. 11,0, ester no. after acetylation 40,7, soluble

¹⁾ The famous "Cypress of Montezuma" in the cemetery of Santa Maria del Tule near Oaxaca belongs to the same variety. It is said to be 130 ft. high, the trunk to have a circumference of 98 ft. De Candolle estimated its age at 6000 years, Humboldt at 4000.

in 2,6 vol. and more of 70 per cent. alcohol. From the low ester and acetylation numbers it is to be inferred that the oil contains but small proportions of saponifiable and alcoholic constituents.

With regard to an oil of *Artemisia Herba-alba* previously examined by E. Grimal, compare our Report October 1904, 13. This oil differs entirely from the one now under review, which may without further enquiry be set down to the fact that *A. Herba-alba* shows very wide variations. Several varieties exist which have been regarded as separate species by many authors; J. Gay, for instance, describes the variety above-mentioned as *A. Oliveriana*.

Pharmacopœias.

The British Pharmaceutical Codex 1907.

In our previous April Report¹⁾ we expressed ourselves in detail on the subject of the requirements fixed in the British Pharmaceutical Codex, published in the year 1907, for essential oils and their constituents. A similar review has now been published by C. T. Bennett¹⁾ in the *Pharmaceutical Journal*. Without entering into further details we will content ourselves with the observation that our opinions differ from those of Bennett on many points, and that we maintain our former criticism in every particular. We recommend that in judging oils our observations should be taken as the basis, as otherwise erroneous conclusions might perhaps be arrived at concerning this or that oil.

Swedish Pharmacopœia.

(Pharmacopœa suecica, ed. IX.)

On January 1st a new edition (the ninth) of the Pharmacopœia came into force in Sweden. Unfortunately we were unable to discuss it in our last Report, before the actual date when came into force because although we ordered a copy of the book in good time, it only reached us in November 1908. So far as concerns the articles in which we are specially interested, we may repeat what we wrote when discussing the eighth edition²⁾, namely that in their statements as to properties and tests the editors have everywhere been careful to take account of the actual state of science. But we wish to lay special stress upon the fact that the criticisms which we then offered have throughout been taken into consideration in the new Pharmacopœia, so that there is little left for us to say concerning the

¹⁾ Report April 1908, 134.

²⁾ Report April 1902, 68.

present edition. Unfortunately it is true that one important alteration, that with regard to the determination of the boiling points, has not been carried out. At the time we pointed out specially that, in order to obtain accurate results, the whole of the mercury column concerned must be surrounded by the steam of the liquid. The barometric pressure must also be considered. But in the "allmänna föreskrifter" (general rules) nothing is said as to this, on the contrary, the prescriptions relating to the determination of the boiling point have been reprinted without alteration from the eighth edition; which lays it down that the thermometer should be so arranged that the mercury bulb is placed immediately below the lateral delivery tube. Under such conditions there can be no doubt that in many boiling point determinations only a portion of the mercury column will be exposed to the steam from the liquid and that the thermometer, in such cases, will be quite unable to register the actual boiling point, so that the results will require correction. In order to obtain accurate values the thermometer must be fixed in such a manner that the degree of the boiling point is slightly above the delivery tube, but care should be taken that the mercury bulb does not protrude into the bulb of the flask, or even into the liquid itself. Shortened thermometers are the best adapted for tests of this kind. It is almost impossible to lay too much stress upon the importance of this condition, for in most cases where objections are raised it is found that claims based on an alleged improper boiling point have their ground in a defective testing method.

No oil has been newly introduced into the Pharmacopœia, while oils of fennel and mace are no longer official.

The enumeration of the separate essential oils is prefaced by a short general chapter on properties and method of keeping, as well as on tests for alcohol and fatty oil.

Among the alcohols, a change has been made in *Spiritus dilutus*, its alcoholic strength having been raised, the following being the strengths now prescribed:

- Spiritus concentratus* (Sprit): 90,3 to 91 %,
- „ *dilutus* (Utspädd sprit): 69,6 to 70,5 %,
- „ *tenuis* (Svag sprit): 48,4 to 50,6 %.

By "parts" the Pharmacopœia understands "parts by weight".

Anethol (*Anetholum*). The solid constituent of oil of anise¹). A white, leaf-like, crystalline mass, which melts into a colourless or faintly yellow²), somewhat thickish liquid; $d_{25^{\circ}}$ 0,984 to 0,986, $n_D^{\circ} \pm 0^{\circ}$, congeals at about 20° ³) and melts at 21 to $22,7^{\circ}$, b. p. 233 to 234° , gives a clear, neutral solution with less than 2 parts of *spiritus conc.* at 20° ⁴).

Anethol is to be dispensed in lieu of anise oil and of fennel oil.

¹⁾ Anethol from star anise oil or fennel oil is completely identical with that from anise oil.

²⁾ Good anethol is always colourless.

³⁾ The congealing-point of a good preparation lies between 21 and 22°; when the oil is imperfectly kept it falls considerably. Compare Report October 1904, 42.

⁴⁾ In order to dissolve 1 vol. anethol, 2 to 3 vol. 90 per cent. alcohol are required.

Camphor (*Camphora*). A white, fatty, lustrous, tough, crystalline mass, m. p. 175 to 177°, b. p. 204 to 208°; burns with a highly luminous flame; sparingly soluble in water, readily soluble in alcohol, ether, chloroform, fatty and essential oils. Camphor should be completely soluble in *spiritus conc.* and, when slightly warmed, should sublime without leaving a residue.

Carvone (*Carvonum*). Colourless or faintly yellow; d_{15° 0,963 to 0,966; α_D to the right¹⁾; b. p. 229 to 230°; soluble in any proportion in *spiritus conc.* and at 20° in 20 parts *spiritus tenuis*; test with ferric chloride. Carvone is to be dispensed in lieu of caraway oil.

¹⁾ The rotation lies between + 57 and + 60°.

Cinnamic aldehyde (*Cinnamalum*). Yellowish; d_{15° 1,054 to 1,056¹⁾; $\alpha_D \pm 0^\circ$; congeals when strongly cooled and melts again at — 7,5°; b. p. about 252° under partial decomposition; soluble in any proportion in *spiritus conc.*; nitric acid test; silver mirror; ferric chloride reaction; test for chlorides. Cinnamic aldehyde when heated with a solution of bisulphite of sodium should dissolve completely. Cinnamic aldehyde is to be dispensed in lieu of cassia oil.

¹⁾ In our own preparations, we have observed up to 1,058.

Eucalyptol (*Eucalyptolum*). Colourless or faintly yellow¹⁾ d_{15° 0,928 to 0,930; $\alpha_D \pm 0^\circ$; b. p. 176 to 177°; when strongly cooled down, it congeals to a white, crystalline mass which melts at — 1°²⁾; soluble in any proportion in *spiritus conc.*; reaction with bromine. Eucalyptol is to be dispensed in lieu of cajeput oil and eucalyptus oil.

¹⁾ A good article is always colourless.

²⁾ The m. p. lies between + 1 and + 1,5°. Compare Report October 1907, 49. Congelation should, if necessary, be induced by rubbing the side of the vessel with a glass rod.

Eugenol (*Eugenolum*). Bright yellow; darkens in course of time; d_{15° 1,070 to 1,074; $\alpha_D \pm 0^\circ$; b. p. 251 to 253°; soluble in any proportion in *spiritus conc.* and in ether, also in 2 vol. *spir. dil.* With an equal volume of caustic soda solution (25% NaOH) eugenol should yield a solid crystalline mass. Ferric chloride reaction.

Lavender Oil (*Aetheroleum Lavandulae*). Bright yellow or bright greenish yellow; d_{15° 0,885 to 0,895; α_D slightly to the left¹⁾. Sap. no. not below 90²⁾; soluble in any proportion of *spiritus conc.*

¹⁾ The rotation lies between — 3 and — 9°.

²⁾ Corresponds to a minimum content of 31,5% linalyl acetate.

Lemon Oil (*Aetheroleum Citri*). Bright yellow; $d_{15^{\circ}}$ 0,855 to 0,861¹⁾; $\alpha_D^{20^{\circ}}$ $+58$ to $+65^{\circ}$; usually not quite clearly soluble in 5 parts of *spiritus conc.* Oil of lemon should only have a slight deposit and give no strongly acid reaction.

¹⁾ Pure oils of less than 0,857 sp. gr. are very rare, and we have only on very exceptional occasions observed a sp. gr. so low as 0,856, never one below that figure.

Menthol (*Mentholum*). Colourless, brittle crystalline needles, almost insoluble in water, readily soluble in *spiritus conc.*, ether, chloroform and fatty oils; m. p. 43° ¹⁾; b. p. 212° ²⁾; 0,1 g. menthol, when heated on the water-bath, should evaporate without leaving a residue.

¹⁾ The m. p. lies between $43,5$ and $44,5^{\circ}$.

²⁾ Menthol boils at 217° when the mercury column of the thermometer is wholly surrounded by the vapours. See Introduction.

Mustard Oil (*Aetheroleum Sinapis*). Colourless or pale yellow; $d_{15^{\circ}}$ 1,016 to 1,025¹⁾; $\alpha_D \pm 0^{\circ}$; soluble in any proportion in *spiritus conc.*, ether, benzene and carbon disulphide. On distillation the bulk should pass over between 147 and 152° , and the sp. gr. of the first, as well of the last, fraction should not differ materially from that of the original oil; thiosinamine and sulphuric acid tests; ferric chloride reaction; isothiocyanallyl content 82,3 to 100%²⁾.

¹⁾ We have found pure oils to have as low a sp. gr. as 1,014.

²⁾ The present edition of the Pharmacopœia prescribes a test which differs from the older method to this extent that the mustard oil is no longer to be left standing with the ammoniacal silver solution for 24 hours at normal temperature, but only for 1 hour at a temperature of about 75° . See our Report April 1908, 70.

Peppermint Oil (*Aetheroleum Menthae piperitae*)¹⁾. Colourless, yellowish or faintly yellow green; $d_{15^{\circ}}$ 0,90 to 0,92; α_D to the left; 1 part of oil should give a clear, or at most a faintly opalescent solution with 3 to 4 parts of *spiritus dil.* Iodine reaction²⁾.

¹⁾ English as well as American oil answers these requirements.

²⁾ Reactions of this kind are out of date and purposeless.

Rosemary Oil (*Aetheroleum Rosmarini*). Colourless or bright greenish yellow; $d_{15^{\circ}}$ 0,90 to 0,92; α_D to the right; soluble in 0,5 parts of *spiritus conc.*

Sandal Oil (*Aetheroleum Santali*). Bright yellow, somewhat viscid; faintly acid reaction; $d_{15^{\circ}}$ 0,975 to 0,985; $\alpha_D^{20^{\circ}}$ -17 to -20° ¹⁾ soluble in any proportion in *spiritus conc.* and in from 5 to 6 parts of dilute alcohol.

¹⁾ As we have been able to observe in our own, normal distillates, the rotation is occasionally a little less. Compare Report October 1905, 64.

Thymol (*Thymolum*). Colourless, transparent crystals, soluble in water (1100 parts), glycerin (100 parts) and very readily in *spiritus conc.*, ether and chloroform, also soluble in fatty and essential oils and in soda solution; m. p. 50 to 52° , b. p. 228 to 230° ¹⁾. When solid thymol sinks in water; in the molten state it floats upon it; 0,2 g. of

thymol should evaporate on the water bath without leaving a residue; identity-reaction; test for phenol.

¹⁾ Thymol boils between 233 and 234° when the mercury column is entirely surrounded by the vapours. Compare Introduction.

Turpentine Oil, crude (*Aetheroleum Terebinthinæ crudum*). Colourless or faint yellow; $d_{15^{\circ}}$ 0,860 to 0,875; b. p. 150 to 162°; should have no empyreumatic smell.

Turpentine Oil, purified (*Aetheroleum Terebinthinæ depuratum*). Colourless; $d_{15^{\circ}}$ 0,860 to 0,870; b. p. 155 to 162°; soluble in 10 to 12 parts of *spiritus conc.*; 5 g. of oil when allowed to evaporate on the water bath must leave no weighable residue; when 25 cc. oil are shaken with 5 cc. *spiritus conc.* and 2 drops of phenolphthalein solution, the alcoholic layer should assume a definite red colour when 0,3 cc. $\frac{1}{10}$ normal potash solution is added.

Chemical Preparations and Drugs.

Apiol. It will be remembered that this body has been introduced into the new French Pharmacopœia of 1908¹⁾ which is to come into force on 15th May of the current year²⁾. For the present we have no means of estimating the total annual requirements of the French pharmacies in this article, but judging by the enquiries already received we are disposed to conclude that it is much in excess of the possible production. So far we have just managed to find enough raw material wherewith to produce the slight quantity of apiol for which a market could be found, but we greatly doubt if enough raw material will be available in case the demand for the article should increase materially. It would have been well if the editors of the Pharmacopœia in question had obtained sufficient information on this point beforehand.

Civet. We have received some few small lots of exceptionally fine quality, which we commend to the special notice of connoisseurs of this important perfume. We have in stock original horns of almost all sizes. Some parcels which were offered in Hamburg and Marseilles have turned out to be heavily adulterated, and it is particularly desirable to buy this article only from proved trustworthy suppliers, who are able to give satisfactory guarantees as to original quality.

Coumarin. Since the selling prices have been regulated by a syndicate, business runs a normal course, and although at the low prices ruling it is not possible to make large profits, the ruin which

¹⁾ Report November 1908, 144.

²⁾ Compare the present Report, p. 8.

threatened to overtake this important perfume as a result of persistent price-cutting has been averted, at any rate for some time to come.

According to a report in the journal *Der Seifenfabrikant*¹⁾, the fruit of *Myrospermum frutescens* Jacq. (N. O. *Papilionaceæ*), which has an odour of coumarin and is used in Venezuela as a specific against rheumatism, yields, when extracted with ether, 47⁰/₁₀ of a viscid brown balsam, known as sereipo balsam. This balsam dries up rapidly, acquiring a resin-like appearance. Boiled with water, it yields a crystalline substance of the m. p. 207 to 208°, which was said to be coumaric acid. The saponified balsam boils at from 220° upwards, and decomposes during the boiling.

For the pharmacological behaviour of coumarin, see p. 115.

Menthol. We refer to the statements under the heading of Japanese peppermint oil on p. 78.

Musk, Tonquin. As a result of the scarcity of stocks towards the end of last season, the first arrivals of the new supply were being awaited with great impatience. These arrivals were placed upon the market as early as the month of November, and found buyers at good prices, in spite of their faulty quality. An improvement in the quality of the supplies occurred only in December, but “blue-skins”, the most suitable kind for “graining”, were almost entirely wanting. Every parcel which arrived at Shanghai, no matter what its classification, found ready takers at firm prices. France continues to occupy the first position as purchaser. The musk trade in Europe has gradually become centred in Paris and the figures given in the table below do not even approximately indicate the consumption in England and Germany, as only the direct shipments are recorded in it. A large part of the quantity given under the heading “Paris” ultimately finds its way to the two neighbouring countries.

Exports from Shanghai, from 1st January to 31st December 1908:

Year	To Paris	To London	To New York	To Germany and Austria	Total
	Catties	Catties	Catties	Catties	Catties
1908	666	37	211	9	923
1907	829	57	337	37	1260
1906	670	8	414	45	1137
1905	378	83	387	40	888
1904	722	76	366	52	1216

¹⁾ *Der Seifenfabrikant* 29 (1909), 61.

Safrol. The quotations for this important article have preserved their previous level during the last few months and, as heretofore, the principal share of the business has been concentrated in our hands. We can supply any quantity required, and in the case of large requirements we are always prepared to make special offers.

Thymol. No turn for the better whatsoever can be noted in the distressed condition of this important preparation. For the Hamburg firms, who have made it their business to ruin the article systematically, the condition towards which trade has been shaping is all the more unpleasant because ajowan seed has considerably declined in price, and large stocks of expensive material still remain to be worked up. We have succeeded in making very favourable purchases of seed in India, and shall be glad to submit to anyone interested in the article special offers for large parcels or for future delivery.

Notes on recent research work concerning terpenes and terpene derivatives.

General.

According to an article quoted from the *Bulletin mensuel de l'Office du Gouvernement Tunisien*¹⁾ the cultivation of essential oil yielding plants in Tunis has not attained that importance which properly belongs to it, because of the competition of Grasse and Germany and also because heavy customs duties are levied in France on essential oils. Nevertheless, in the peninsula of Cap-Bon, especially at Hammame and Nabeul, the natives grow geranium, tuberose and bitter orange on a small scale.

Pelargonium capitatum ("géranium rosat") is often cultivated for the manufacture of spurious rose oil. Oil prepared in a primitive manner sells at from 15 to 20 fr. per kilo, while if it is distilled in the proper way as much as 30, and occasionally even 40 fr. is paid for it. Cuttings cost about 2 fr. a thousand. The average cost of the necessary tilling of the soil is 40 fr., of the planting 35 fr., and of the working of the ground, which has to be done three times, 30 fr. The crops, which are gathered in April, August, and October, involve a total expenditure of about 90 fr. A hectare produces about 20 kilos of oil.

Orange flowers. For the preparation of neroli oil, the variety *bouquetier de Nice* is the most suitable. Petitgrain oil, which is worth little, is obtained by distilling the leaves. In Tunis the flowers are not distilled, but only sold. According to its age, a plantation containing 150 trees per hectare may produce from 2500 to 4000 kilos of flowers. These are bought up by distillers at 30 fr. or more, and on exceptional occasions at up to 50 fr. per 50 kilos. For some time past a French firm has been planting the *bouquetier de Nice* variety at Nabeul, while another firm buys the entire fresh flower crop there every year.

Acacia Farnesiana occurs in varieties with scented and with scentless flowers. Even in the dry districts it flourishes very satisfactorily. The plant requires only little water and hardly any attention, and so far as the quantity of flowers produced is concerned, its cultivation might yield a good supply for the perfumery industry.

Jasmine. *Jasminum grandiflorum* is preferred for the preparation of the perfume. The plant is grown from cuttings, which are placed at distances of $1\frac{1}{2}$ m. The flowers are not distilled in Tunis, but they are an article of commerce, and sell at 2 to 3 fr. per kilo. In

³⁾ Journ. de la Parfumerie et Savonnerie 22 (1909), 6.

a well-kept plantation the product is about 40 kilos of flowers per 1000 plants.

Eucalyptus. The distillation of eucalyptus leaves is practically not carried on at all, although, at any rate with *Eucalyptus globulus*, from 90 to 120 fr. per year per hectare might be realised.

Thyme. The oil is obtained from *Thymus algeriensis*, a familiar plant in Tunis, which grows rather thickly in the districts of Zaghouan, Pont-du-Fahs, Oudan, etc. The plant is distilled in a similar way to geranium and yields 1,5% of oil.

Mint. The oils are obtained by distillation of the leaves of pennyroyal and peppermint. These two very hardy plants can easily be cultivated in Tunis and need little care. 1000 kilos of leaves produce from 2 to 3 kilos of oil of a value of about 85 fr.(?) per kilo.

Tuberose. The tubers of *Polyanthes tuberosa*, N. O. *Liliaceæ*, are planted in rows at a distance of 30 cm. 1000 plants produce from 25 to 30 kilos of flowers, which sell at 2 to 2,50 fr. per kilo.

In 1907 Tunis imported 3423 kilos of essences and essential oils, to the value of 33122 fr.; the exports amounted to 14862 kilos, valued at 46127 fr.

Bibliography.

Otto Wallach, the well-known originator of modern terpene chemistry, has published the result of his 25 years' pioneering investigations in a comprehensive volume, entitled *Terpene und Campher. Zusammenfassung eigener Untersuchungen auf dem Gebiet der alicyclischen Kohlenstoffverbindungen*¹). (Terpenes and Camphors. Repertory of my own Researches in the Domain of the Alicyclic Carbon combinations.) This work is by no means a mere reprint of every single treatise published by the author, who has written far more than a hundred such, but contains the whole material scattered throughout these publications, arranged systematically in review from uniform points of view.

In the general part of the work, Wallach first explains the principles upon which he has proceeded in his investigations, after which he deals with the mutual relations which he has found to exist between the separate members of the terpene series. In addition to the isomerisation processes, which are particularly characteristic of the series, all the numerous conversions which have been observed are recorded, arranged in tabular form as hydrocarbons, ketones, alcohols and oxides. Then follows an exposition of the methods of research which have been applied by Wallach with such extraordinarily prolific results. This section is divided into chapters on addition reactions in saturated and unsaturated combinations; reactions of interchange and abstraction;

¹) Leipzig 1909, Veit & Co.

decomposition by oxidation, with notes on the specific behaviour of the various oxidising agents; reactions of condensation and ring-formation; and the rupture, and extension of ring-systems. After an exposition of the origin and behaviour of the most important types of combinations which are met with in practice, we have chapters on physical properties, constitutional relations, syntheses, division and nomenclature. An extensive review of all the combinations which have been examined, systematically arranged, and containing accurate and complete references to the literature of each combination, brings the general part of the work to a close.

The second, or "special" section contains, in concise form, the vast positive experimental material dealt with in Wallach's publications. This is arranged in the 19 principal groups which have, in practice, served as bases of investigation, viz., Pinene, Pinol, Limonene, Terpinolene, Terpene and Terpineol, Cineol, Carvone, Eucarvone, Pulegone, Menthone, Monocyclic Ketones, Terpinene, Phellandrene, Sylvestrene, Sabinene, Thujone, Fenchone, Camphor, and Sesquiterpenes. Each of the principal divisions in this section is preceded by an introductory chapter giving a brief general review of the particular field covered.

Wallach's work affords ocular demonstration of the wideness of the field which this famous investigator has thrown open to scientific research, and also shows how large a share he has had in its development. It will be of special interest and great usefulness not only to his pupils, to whom it is dedicated, but to all other workers in this branch of science.

The third part of the second volume of the third edition of *Posts Chemisch-technische Analyse* which has been edited by B. Neumann, contains a chapter on essential oils by J. Helle. The author first describes briefly the manner of testing the raw materials and then enters in detail into the physical and chemical testing of essential oils, in the course of which, besides dealing with the generally applicable methods, he considers a few special processes, such as, for example, the determination of cineol, hydrocyanic acid, isothiocyanallyl, etc. The detection of the most common adulterants is also discussed at length. A tabular review of the properties and composition of the principal essential oils brings this little work to a close. The book will no doubt prove a good and reliable guide for technical chemists in the analysis of essential oils.

A second edition of Ernest J. Parry's well-known work *The Chemistry of Essential Oils and Artificial Perfumes* has been published (Scott, Greenwood & Son, London, 1908), with the object of recording

the progress which has been made in the investigation of essential oils since the first appearance of the book in 1899. The enormous output of publications dealing with essential oils has necessitated a considerable enlargement of the book, which finds expression in the growth of the volume up to 546 pages, as compared with 411 pages in the first edition. The work concerns itself chiefly with laboratory practice, and for this reason it deals only briefly with the chemistry of the various constituents and the method of preparation of the oils, while on the other hand a great deal of space is devoted to the description of the properties and to the testing of oils. The leading commercial oils in particular are discussed at great length, special stress being laid upon the detection of adulterations and upon the eventual quantitative determination of the constituents, which are of value in determining the value of each particular oil. The book contains, for example, detailed information with regard to the determination of citral, cinnamic aldehyde¹), eugenol, cineol, etc. A special chapter is devoted to artificial perfumes. As an appendix to the book there is a chart indicating the specific gravity, rotation, index of refraction and composition of the principal oils, and another showing the requirements of the various Pharmacopœias with regard to essential oils.

Although in certain details we are of different opinion as Mr. Parry, his book must nevertheless be pronounced as, upon the whole, a sound guide for the chemist who is engaged in the investigation of essential oils, and in its new dress it ought to add fresh friends to its old circle.

In a brochure entitled *Les constituants des Huiles Essentielles* (Paris, Alph. Isnard) the author, Marcel Viard²), treats his subject in a concise, summary manner. After a discussion on the general properties of essential oils, with consideration, in parts, of the effect thereon of their chemical composition (which discussion may be regarded as a sort of introduction), Viard first proceeds to draw a general outline of the methods used in the separation of the most important constituents of the oils, and then refers specially to the separate bodies, which he groups according to their chemical properties. In the case of each combination reference is made to the oils which serve as the crude material for its preparation, and methods are given for the quantitative determinations of the oils, insofar as any are known, as well as for the manner of isolating the constituents of the various oils. In the case of the more important combinations there are also data for the purification of the crude product. Viard further gives data for judging the various bodies,

¹) Parry calls our cassia flask "Hirschsohn flask". Compare Report November 1908, 92.

²) We here return thanks to Mr. Viard for courteously sending us a copy of his pamphlet.

the properties and derivatives of which he discusses. This small monograph, which has been written by a practician, should be of special interest to those practically engaged in the business.

The Commercial Products of India (London, John Murray, 1908) is the title of a book by Sir George Watt which, as the author himself states, consists of a synopsis of his own voluminous work *Dictionary of the Economic Products of India*. It goes without saying that in this synopsis regard has been taken to recent research. The volume, which contains 1189 pages, carries out its purpose of giving, in a compressed and concise form, the most important details on the economic products of India. It will probably be welcomed by all who wish to acquaint themselves rapidly with what is most worth knowing on this subject.

We are glad to seize this occasion of expressing our best thanks to the author for kindly presenting us with a copy of the book.

A further series has appeared of J. W. Brandel's¹⁾ discussions on the investigations of essential oils published in the years 1901 to 1903, to which work we have repeatedly referred in the past²⁾.

Analytical.

The method for the determination of the citral content in oil of lemon by the use of hydroxylamine, which was recommended by J. Walther³⁾ and discussed by us in detail at the time⁴⁾, has now been published, in a modified form, by A. H. Bennett⁵⁾. This author uses potash liquor instead of bicarbonate of sodium for averting the evolution of carbonic acid and the loss of hydroxylamine which may result therefrom. The quantity of alcoholic potash used by him is sufficient to liberate from its hydrochloric salt an excess of hydroxylamine in proportion to the citral present, so that a residue of unconverted hydrochloride is left. Bennett proceeds as follows: He dilutes a mixture of 20 cc. of lemon oil and 20 cc. alcoholic (80 per cent. alcohol) $\frac{1}{2}$ normal solution of hydrochloride of hydroxylamine with 8 cc. of alcoholic normal alcoholic potash and 20 cc. strong alcohol, free from aldehyde, and boils for half an hour with reflux-condenser. After cooling, the mixture is diluted with 250 cc. water, part of which is used for washing down the reflux-condenser, and the hydrochloric acid which is still present in the form of hydrochloride of hydroxylamine

¹⁾ Pharm. Review 26 (1908), 371.

²⁾ Report April 1908, 168; November 1908, 155.

³⁾ Pharm. Zentralh. 40 (1899), 621; 41 (1900), 614.

⁴⁾ Report April 1900, 22.

⁵⁾ The Analyst 34 (1909), 14. Quoted from Chem. Zentralbl. 1909, I. 593.

is neutralised, phenolphthalein being employed as indicator. The hydroxylamine which is not in combination with citral is then titrimetrically determined with $\frac{1}{2}$ normal sulphuric acid by ascertaining the final reaction by means of stipple-tests with a very dilute methyl orange solution. A similar course is followed in a blank test without oil of lemon, in order to determine the value of the hydroxylamine solution. The quantity of hydroxylamine which has entered into reaction is calculated from the difference in the cc. of $\frac{1}{2}$ normal sulphuric acid which has been used up in each of the tests, and furtheron, the amount of citral, by multiplying by 0,076. A. H. Bennett has tested the value of the method with pure citral; in the case of oils of lemon the citral content thus determined varied from 4,3 to 5,2 %.

We were unfortunately unable to form an opinion as to the method in time for the present Report, and we therefore limit ourselves here to a mere recapitulation of the process. We shall return to the matter in our next Report.

A method for the colorimetric determination of benzaldehyde in extracts of bitter almonds, which resembles Mac Kay Chace's method for the determination of citral previously discussed by us¹⁾ has been described by A. G. Woodman and E. F. Lyford²⁾. The solution of fuchsin-sulphurous acid required for this purpose is prepared fresh each time in the following manner: 0,5 g. fuchsin is dissolved in water, and sulphurous acid introduced into the solution until the weight has increased by 20 g. when it is further diluted to make 1 litre. In the next stage, alcohol free from aldehyde is employed; this is obtained by taking spirit which has undergone a preliminary treatment with oxide of silver, and diluting it with 25 g. phenylene diamine hydrochloride per litre of alcohol, then passing a strong current of air through it for three hours, and distilling off, rejecting the first 100 cc. Besides this, a standard solution of freshly distilled benzaldehyde in aldehyde-free alcohol (1 mg. in 1 cc.) is prepared. Next, 10 g. of the almond extract are diluted to 50 cc. with aldehyde-free alcohol; 2 cc. of this solution is placed in a colorimeter tube and diluted to 20 cc. Three control-solutions containing respectively 2, 4 and 6 mg. benzaldehyde are then poured into tubes of equal size, all the tubes are brought to a temperature of 15°, the contents quickly diluted with 20 cc. of the fuchsin-sulphurous acid solution, shaken up, and allowed to stand for 10 minutes. As much of the sample-solution is now run off as will make its colour resemble that of one of the control-solutions. As the colour is in proportion to the degree of concentration of the

¹⁾ Report April 1907, 116.

²⁾ Journ. Americ. chem. Soc. 30 (1908), 1607.

benzaldehyde, the proportion of that body which is present may be calculated. The method is said to give accurate results, and to be applicable also to bitter almond oil.

In a paper read by S. H. Baer¹⁾ before the Association of Official Agricultural Chemists on November 8th 1908, the author points out that there is no practical method for the analysis of "terpeneless lemon extract" based upon the determination of the citral content and that consequently an unobjectionable method for fixing standard values for the product in question is rendered very difficult. Officially a content of at least 0,2 % of citral, which must be obtained from oil of lemon, is demanded. As for analytical investigations commercial citral, obtained from lemongrass oil, is mostly used, Baer thinks it desirable that citral from oil of lemon should be taken as the basis for analytical investigations, especially because citral may exist in isomeric forms. Baer goes on to criticise some of the methods proposed for the determination of citral. As the most suitable method he regards one in which the distilling-off of alcohol and water is obviated and in which the small quantities of citral could be separated from the highly diluted aqueous alcoholic solution by means of a solid derivative for gravimetric determination. For this purpose the bisulphite compound or the semicarbazone might perhaps be used. According to the tests carried out by Baer, Chace's method²⁾ is unsuitable in practice, if only because in manufacturing processes the application of chemically pure citral, distilled water, and alcohol free from aldehyde, is of course out of the question. Besides this, it would be impossible to detect any adulteration with other aldehydes, such as acetaldehyde. On these grounds, Baer opposes the official adoption of Chace's method.

On a method for the determination of thujone in liqueurs, see oil of Wormwood, p. 92.

Physical notes.

J. W. Brühl³⁾ has tested instances in which hydrocarbons with conjugated ethenoid-linkings do not show the condition known as "exaltation". As terpinene, which was recognised by Wallach⁴⁾ as a mixture of $\Delta^{1,3}$ - and $\Delta^{1,4}$ -dihydrocymene, showed a normal molecular refraction, whereas the $\Delta^{1,3}$ -dihydrocymene prepared synthetically by

¹⁾ American Perfumer **3** (1909), 205.

²⁾ Journ. Amer. chem. Soc. **28** (1906), 1472; Report April 1907, 116.

³⁾ Berl. Berichte **41** (1908), 3712.

⁴⁾ Liebig's Annalen **362** (1908), 293; Report November 1908, 174.

Harries and Majima¹⁾ showed "exaltation", Brühl expresses the surmise that it is in the well-known faculty of rearrangement of the cyclic unsaturated hydrocarbons that the cause must be sought of the anomalies which have been observed. He furthermore extends his theoretical speculations to recent publications by Auwers and Hesseland²⁾ and also by Zelinsky and Gorsky³⁾. We cannot go into details on the subject here; suffice it to state that in the case of aliphatic compounds through the conjugation of the ethenoid-groups an "exaltation" of molecular refraction and molecular dispersion was invariably observed, the conjugations increasing in number in an ascending degree. According to Brühl the molecular dispersion in particular is a prominent criterion of the constitution.

Pharmaco-Physiological Notes.

E. Rimini and F. Delitala⁴⁾ have carried out pharmacological researches with safrol, myristicin, apiol, and asaron and with their corresponding propenyl combinations and β -nitro-derivatives. All these combinations acted upon the central nervous system of cold-blooded as well as of warm-blooded animals. In the case of the former, small doses of the allyl and propenyl combinations had a marked narcotic effect, while the β -nitroderivatives provoked a characteristic condition of muscular rigidity. Larger doses produced increasing symptoms of paralysis, ending in death. The allyl combinations had the strongest, the β -nitro-derivatives the weakest, toxic effects; the propenyl combinations stood midway between these two. Safrol possessed the greatest toxicity, β -nitro isoapiol the smallest. These differences in behaviour are to be explained by the greater or less absorbability of the substances concerned. In the case of warm-blooded animals internal administration produced vomiting. When hypodermically administered, the liquid substances produced acute, and the solid substances chronic, intoxication, followed in both cases by fatal results. We are unable to enter into details of the investigations here, and for these we refer to the original paper.

J. Hämäläinen⁵⁾ has made experiments on the action of d-, r- and l-camphor on the heart of the frog, which showed that all three of these modifications were almost without effect upon that organ, of

¹⁾ Berl. Berichte **41** (1908), 2516; Report November 1908, 175.

²⁾ Berl. Berichte **41** (1908), 1819.

³⁾ Ibidem 2479, 2630.

⁴⁾ Archivio di Farmacologia e Terapeutica **14** (1908), 295. From a copy kindly sent to us.

⁵⁾ Skandinavisches Archiv für Physiologie **21** (1908), 64. We quote from a copy kindly sent to us.

which the frequency and power of contraction are almost normal. Upon a heart influenced by chloral, d- and r-camphor had an almost equal action, in which the activity of the heart was often permanently excited. Both were also able to remove the condition of inactivity caused by chloral. On the other hand, l-camphor generally produced only a weak excitation of short duration, while in a few instances the action of the heart was improved by the other modifications. The condition of inaction caused by chloral could not be counteracted by l-camphor. In connection with this matter we call attention to the experiments of Langgaard and Maass on the same subject, which we have referred to in one of our earlier Reports¹⁾.

Several investigations have been made of late years into the narcotic action of nutmegs²⁾. F. Jürss in particular, in his paper *Über Myristicin und einige ihm nahestehende Substanzen* (On myristicin and a few allied substances), published in 1904, called attention to the peculiar fact that from 10 to 12 g. of nutmeg oil or mace oil are required in order to produce toxic symptoms in rabbits, whereas a single nutmeg weighing from 4 to 5 g. is sufficient to cause severe symptoms of this kind in man. It had been ascertained that the myristicin which is present in the oil has a toxic action, affecting in particular the liver, its action upon that organ often causing fatty degeneration, as in the case of phosphorus-poisoning. But the proportion of myristicin in nutmegs is so small that their powerful narcotic action must possibly be due to the presence of another constituent. In order to shed light upon this problem, F. B. Power and A. H. Salway have made a most thorough study of the constituents of the nutmeg. We have already on a previous occasion³⁾ reported on the results obtained by them in respect of the essential oil. Further communications by these two authors have now appeared, dealing with the constitution of nutmeg oil obtained by pressure⁴⁾ and of the pressed cake⁵⁾. These communications are completed by numerous physiological experiments carried out by H. H. Dale. We do not propose to enter into details here, but will only state that no alkaloids or proteïnic substances possessing a toxic action were traced. The chief outcome of the investigations has been the determination of the fact that the narcotic properties of the nutmeg are certainly due to myristicin. It may be inferred from this that myristicin is more easily assimilated when in combination

¹⁾ Report April 1908, 176.

²⁾ Compare Report April 1908, 76; November 1908, 161.

³⁾ Report April 1908, 74.

⁴⁾ Journ. chem. Soc. **93** (1908), 1653.

⁵⁾ Americ. Journ. Pharm. **80** (1908), 563.

with other constituents of the nutmeg than in the pure state, and this theory would explain the differences in the behaviour of the oil and of the nutmeg. The lower animals were much less susceptible to the direct action of nutmeg upon the functions of the brain than were human beings. This agrees with the result of observations on other bodies possessing a narcotic action.

The thiozonide of linalyl acetate prepared by H. Erdmann, and referred to in our last Report¹⁾ has been employed by F. Nagelschmidt²⁾ in clinical experiments in cases of psoriasis, cystitis, syphilis and scabies. These experiments showed the thiozonide to be decidedly superior to thiopinol, the solution of sulphur in oil of pine-needles which had formerly been the subject of experiment. The organic combination of the sulphur appears greatly to increase the power of absorption by the skin when the preparation is administered in the form of an ointment or in the bath. Other advantages of the remedy are its agreeable odour, its non-irritant properties, and the possibility of administering it in exact doses. It was used in various forms, such as an alcoholic solution of organic linalyl acetate thiozonide of sodium together with anorganic sodium thiozonate ("thiozone"), in some instances mixed with glycerine, or as a solution in oil of lavender of the pure thiozonide. Details of the cases treated show the effect of the preparation on the separation of sulphuric acid in the urine. From these records it appears that there was a regular and well-defined increase in the total amount of sulphuric acid separated in the urine, while the total amount of sulphur only increased in proportion to the increase of the sulphuric acid.

A. Ellinger³⁾ has ascertained that coumarin, in proper doses, is a useful narcotic for frogs and rabbits, and, in experimental investigations, possesses the advantage of influencing the circulation only very slightly. On the other hand, it proved to be unsuitable for dogs and for man. For details see the original work.

Observations on the symptoms caused by the self-administration of 8 g. of menthol have been made by A. Schwenkenbecher⁴⁾. The familiar prickly sensation of cold in the mouth and throat extended downwards to the œsophagus to the limit of the presence of nerves susceptible to cold; it therefore ceased in the intestinal

¹⁾ Report November 1908, 178.

²⁾ Therap. Monatshefte 22 (1908), 520.

³⁾ Archiv f. exp. Pathol. u. Pharmak. 1908. Suppl.: Schmiedeberg-Festschrift. Quoted from Chem. Zentralbl. 1908, II. 1945.

⁴⁾ Münch. med. Wochenschr. 1908, No. 28. Through Therap. Monatsh. 23 (1909), 58.

canal. Finally the sensation of cold was also transferred to the mucous membrane of the nose and even to the cuticle, but no change of the circulation in the cellular tissue of the skin was observable. It follows that menthol excites the extreme parts of the nervous organs susceptible to, or capable of, transmitting cold, wherever it comes in contact with them.

It has been repeatedly observed that the oil of *Umbellularia californica* Nuttall possesses a pungent odour which stimulates the action of the lachrymal duct, and also produces headache, and it has further been discovered¹⁾ that these unpleasant effects are due especially to the fractions containing umbellulone, a substance which has recently been examined in detail. We have also had occasion lately to observe the action mentioned above when preparing umbellulone, and at our request Prof. R. Kobert, of Rostock, has examined this ketone pharmacologically. We are indebted to the Professor for the following report on the result of his investigations: —

“The action of umbellulone was tried both on warm-blooded and on cold-blooded animals. With frogs it has a central paralysing action upon the nervous system. A 0,05 g. dose suffices to paralyse medium-sized, vigorous specimens of *Rana esculenta* within 15 minutes, causing them to lie prone as if in death and to be irresponsive to any excitants. But the motoric nerve cylinders continue to be responsive to the electric current, and the heart continues to beat for several hours, when its action slowly ceases. A dose of 0,025 g. also induces complete paralysis, but in this case recovery takes place after an interval of some hours. Neither large nor small doses produce convulsions. 1 g. of umbellulone injected into a small rabbit weighing 570 g. produced symptoms resembling intoxication in the course of 15 minutes. After a further interval of 10 minutes it lay as if in a profound sleep and was almost irresponsive to excitants. At first respiration and cardiac action continued normal. 40 minutes after the injection the respiration and the beating of the heart grew fainter and 50 minutes after the injection the animal died without any symptoms of excitation. This experiment led to the idea of using umbellulone as a narcotic, and a much smaller dose was tested for possible subsidiary effects. As small a dose as 0,4 g. per 1500 g. rabbit (hypodermically) produced dislike for food lasting several days and albumen in the urine. In contact with blood-corpuscles, umbellulone causes hæmolysis, even when greatly diluted. In view of these facts the use of umbellulone in therapy is probably out of the question.”

¹⁾ Heany, Americ. Journ. Pharm. **47** (1875), 105; Pharmaceutical Journal III. **5** (1875), 791; Stillman, Berl. Berichte **13** (1880), 630; Power and Lees, Journ. chem. Soc. **85** (1904), 629. Report October 1904, 87.

Prof. Kobert reserves further investigations (especially as regards the question to what extent the action of umbellulone in cases of acute poisoning may resemble that of pulegone in causing pronounced organic changes, akin to those caused by phosphorus poisoning) and also comparative tests in respect of its antiseptic properties.

For notes on the pharmaco-physiological behaviour of p-, m-, and o-thymol, see p. 136.

Phyto-physiological Notes.

Reference may here be made to a lengthy treatise by O. Tunmann¹⁾ entitled "Contribution to the knowledge of the cuticular glands", because some volatile oils owe their existence to these glands. The author discusses in the first place the essays dealing with the forming of secretions, and concludes that there is a correspondence between the formation of secretions in the vegetable Kingdom and the same process in the glandular tissues of the human skin, that is to say, the sebaceous glands and gland-surfaces. The secretive matter is only found outside the glandular cells, as it is divided from the plasma of the secernating cells by a wall of cellulose which is always visible. As it has been proved that the secretion occurs only in the subcutaneous gland-sacs, it must have originated there, and must have been produced by a resin-secreting membrane. The first investigator who discovered the resin-secreting layer was Tschirch, who gave to this part of the membrane the name of "resinogenous layer" (resinogene Schicht). The determination of this layer in the glands of the skin is easier when the material worked upon has been soaked for one or two months in concentrated aqueous solution of acetate of copper, which hardens it. If fresh material is employed, the *modus operandi*, according to Tunmann, should be as follows: Delicate horizontal cuts should be made, so that the glands may be inspected from above, or in diagonal section. Next add an aqueous solution of chloral hydrate (10, 20, 30 or 40%). If the layer should not yet be visible the strength of the solution should be increased by degrees until the major part of the resin has been dissolved. Now exert with the finger a gentle pressure upon the side of the covering glass. This will burst the cuticle and push it aside, while the resinogenous layer will be placed either upon the top of the secernating cells, or, separated from the latter, at the side of the gland-head. It is not necessary that all the resin should be dissolved. Staining with diluted tincture of alkanet will show the residual resin, leaving the resinogenous layer uncoloured.

¹⁾ Berichte d. deutsch. pharm. Ges. 18 (1908), 491 to 540.

It is very easy to find the layer in dried vegetable material (drugs). In a few cases the cuticle will here be found to have burst, and the secretion to have run out, the layer being thus disclosed without further trouble; in other cases it is necessary to use chloral hydrate solution, as mentioned above.

By the aid of the processes described, Tunmann succeeded in discovering the resinogenous layer in all the plants examined by him. In the course of his investigations he was able to determine various typical forms of the layer. These he divides into three principal types: the rod-type (*Viola*, *Fraxinus*, *Alnus*), the vacuola-type (*Salvia*, *Hyssopus*) and the mesh or grille type (*Rhododendron*, *Azalea*).

The cuticle of the glands of the skin is partly enlarged by stretching, partly by subsequent development. Its principal purpose is unquestionably to prevent a too rapid exudation or loss of the secretions. In the case of all the persistent glands of the *Labiatae*, *Pelargoniae*, *Compositae* etc., all of which possess a strong cuticle, a continuous volatilisation of essential oil takes place throughout the whole life of the plant, that is to say, a loss of the volatile portions of the secretion by way of the cuticle. In the course of this process the chemical composition of the essential oil must of course undergo some modification, but it does not reach a demonstrable process of resinification, because new volatile portions are continuously being formed. Only in autumn, when the period of growth is reaching its end, this formation of volatile constituents ceases, and the remainder of the oil resinifies. Thus it is that autumnal leaves are found to contain in lieu of the usual, almost colourless, highly refractory essential oil, a dark yellow, partly crystalline, partly amorphous, somewhat sparingly soluble lump of resin.

Generally speaking, the view has been accepted that vegetable secretions are decomposition products formed in the course of the metabolism, but Tschirch breaks a lance for the theory that these secretions are built up to serve quite definite and various biological objects, and in this view he is supported by Tunmann.

In some cases, the formation of essential oil in the plant begins at a very early stage, in fact, before the gland has attained its full development.

In opposition to Charabot, Tunmann shows that the constant change in the chemical composition of vegetable essential oils during the progress of the development of the plant, is chiefly due to the continuous evaporation of the more volatile parts. He agrees with Charabot in deducing, from pharmaco-physiological considerations, that plants in flower cannot yield so valuable an oil as can the young spring leaves.

Hydrocarbons.

Ocimene. C. J. Enklaar has subjected ocimene (the aliphatic hydrocarbon which had already been examined by him several times)¹⁾, and some of its derivatives, tho the action of ozone.²⁾ When ocimene was ozonised in carbon tetrachloride solution there was formed an oily ozonide of variable composition, possessing the properties of an aliphatic ozonide. In addition there were formed products of decomposition, which either separated out in the form of a sublimate, or were kept in solution by the carbon tetrachloride. They were partly of a crystalline, partly of a liquid, constituency. The liquid products of decomposition appeared to consist of methylglyoxal; the solid products were made up of trioxymethylene (m. p. 164 to 166°), the polymer of formaldehyde, and of acetone peroxide (m. p. 131°). When allo-ocimene was ozonised, trioxymethylene and acetone peroxide were likewise obtainable, but in this case the ozonide itself appeared to be a combination containing less than 10 carbon atoms. Dihydro-ocimene, $C_{10}H_{18}$, yielded an oily ozonide which was soluble in carbon tetrachloride, but insoluble in petroleum ether. The single ozonides were decomposed by water, in the course of which process ocimene and allo-ocimene ozonides gave off dioxide of carbon. The aqueous solution of the products of decomposition of ocimene ozonide contained a polymer of methylglyoxal (as was shown by a conversion into the proper substance), of which the phenylhydrazone melted at 145°. Furthermore, the presence of acetone, acetic acid and malonic acid could be proved. Probably, malonic aldehyde had also been formed, the pronounced red coloration which was given with ferric chloride, and the formation of a semicarbazone melting at 245°, pointing to this conclusion. On the other hand, no lævulic acid, oxalic acid, or lævulic aldehyde could be detected. The following decomposition products of allo-ocimene had been formed: acetone, an aldehyde (phenyl hydrazone, m. p. 230°), pyrrolic acid (phenyl hydrazone, m. p. 169°), and very probably also malonic aldehyde. The ozonide of the dihydro-ocimene yielded as products of decomposition principally lævulic acid (b. p. 148 to 149° at 14 mm. pressure); also acetone, acetic acid and probably lævulic aldehyde and malonic aldehyde. A determination of the molecular dispersion of the three above-named hydrocarbons showed considerable deviations from the values calculated.

¹⁾ Report October 1904, 14; April 1906, 109; October 1907, 113; November 1908, 153.

²⁾ Recueil des trav. chim. des Pays-Bas 27 (1908) 422. From a copy kindly sent to us.

Pinene. By oxidation of d- and l-pinene of high rotatory power, Ph. Barbier and V. Grignard¹⁾ obtained the optically active forms of pinonic and pinic acids. l-Pinene from French turpentine oil (b.p. 155 to 157°, α_D — 37,2°; 157 to 160°, α_D — 32,3°) was oxidised with permanganate. From the product of oxidation, which (after elimination of the volatile acids and of nopinic acid) boiled at 189 to 195° under 18 mm. press., l-pinonic acid separated out in long crystalline needles, which, after filtration by the suction pump and re-crystallisation from a mixture of ether and petroleum ether, melted from 67 to 69°. The acid was easily soluble in water and ether, fairly soluble in chloroform, and almost insoluble in ligroin. Its specific power of rotation was determined to be $[\alpha]_D$ — 90,5° in chloroform solution. Oximation produced two oximes; one lævogyre, m. p. 128°; and the other dextrogyre, m. p. 189 to 191°, corresponding to the β - and γ -pinonic acid oximes described by v. Baeyer²⁾, which this investigator obtained from oily pinonic acid. By oxidising l-pinonic acid with hypobromite, active pinic acid, $C_9H_{14}O_4$, was produced. This possessed the following characteristics: b. p. 225° at 17 mm. press., m. p. 135 to 136°, $[\alpha]_D$ + 7,10° in acetone solution. The oily parts filtered off from l-pinonic acid proved to be a mixture of this acid with racemic pinonic acid, the latter melting at 104 to 105°.

d-Pinene from myrtle oil (b. p. 155 to 158°; d_{40}^{140} 0,8635; n_D 1,46977; $[\alpha]_D$ + 39,4°) yielded upon oxidation a mixture of racemic and d-pinonic acids. The latter melted at 67 to 68° and showed the same properties as the acid described above, except as regards its specific rotatory power, which was found to be $[\alpha]_D$ + 89,0°. By mixing the two active pinonic acids the inactive form, m. p. 104°, was obtained. Oximation produced the two oximes corresponding to the above. A preparation obtained by Tiemann from α -dihydroxy dihydrocampholenic acid by means of distillation, and described as l-pinonic acid (m. p. 98 to 99°; oxime m. p. 147°) possibly represents, according to Barbier and Grignard, a stereo-isomeric acid.

With reference to the foregoing we wish to point out that research upon the same subject has been in progress in our laboratory. We were the first to obtain l-pinonic acid by oxidation of l-pinocamphone from oil of hyssop, and described it briefly in a preliminary communication³⁾.

We had reserved further investigation of the compound to ourselves. In order to place beyond a doubt the characteristics of our acid by comparing it with the dextrorotatory acid, and inspired by the same con-

¹⁾ Compt. rend. **147** (Oct. 5, 1908), p. 597.

²⁾ Berl. Berichte **29** (1896), 2786.

³⁾ Report April **1908**, 58. Chem. Zentralbl. **1908**, I. 1840. May 20.

siderations upon which Barbier and Grignard proceeded, we had oxidised a pinene of high rotatory power from Greek turpentine oil (b. p. 156° ; d_{15}° 0,8642; n_{D20}° 1,46565; $[\alpha]_D +47,73^{\circ}$) and had likewise obtained d-pinonic acid. The constants ascertained by us for both acids agree with the indications given by Barbier and Grignard. For the *lævogyre* acid we found: m. p. $69,5$ to 70° and $[\alpha]_D -90,36^{\circ}$ in chloroform solution; for the *dextrogyre* acid: m. p. 68 to 69° and $[\alpha]_D +88,2^{\circ}$ in the same solvent. We purpose, later on, to publish elsewhere our investigations into these bodies.

According to P. Golubew¹⁾, pinene nitroso-chloride, by treatment with piperidine, can be made to yield, besides the nitrol-piperidide (m. p. 118 to 119°), nitroso-pinene (m. p. 134 to 135°) by the splitting off of hydrogen chloride. As Wallach²⁾ showed long ago, the reaction, when other bases, such as diethylamine, are used, takes place chiefly in the last-named direction.

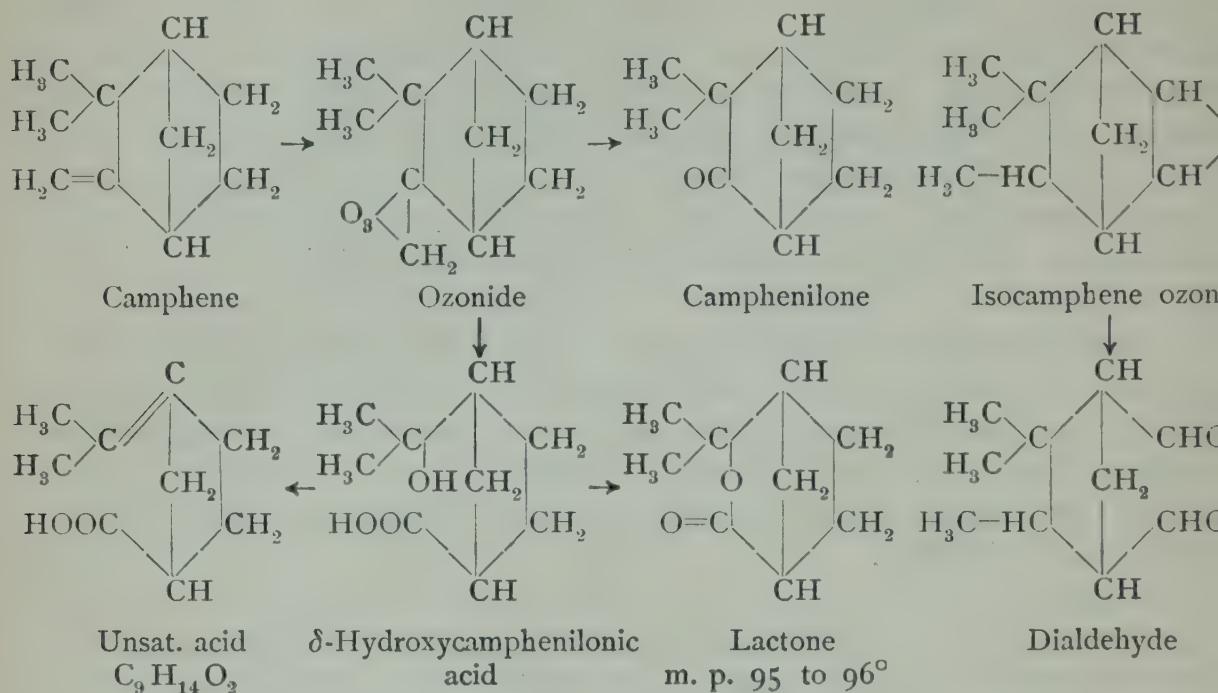
Camphene. While oxidising crude camphene, F. W. Semmler³⁾ obtained practically only a single oily ozonide $C_{10}H_{16}O_3$, which, however, could be split up in two different ways. In one case it yielded 30% of camphenilone $C_9H_{14}O$ (m. p. 40° ; d_{38}° 0,9705; semicarbazone, m. p. 223°) of which the oxime (m. p. 109° ; b. p. 128 to 129° at 14 mm. press.) was converted through the nitrile into camphoceanic acid (b. p. 145 to 146 at 11 mm. press.; d_{20}° 1,020; n_D 1,4862). By the other method there was obtained from the ozonide a syrupy saturated hydroxy acid $C_9H_{16}O_3$ (δ -hydroxycamphenilonic acid) which by means of distillation *in vacuo* was converted into an also saturated, well-crystallising lactone $C_9H_{14}O_2$ (m. p. 95 to 95° ; b. p. 126 to 128° at 10 mm. press.). In addition to the above method, the process of splitting-off of water could be carried out in another way, resulting in a mixture of a saturated and a non-saturated acid, both of them possessing the formula $C_9H_{14}O_2$. Now, the formation of camphenilone from semicyclic camphene can be understood without further explanation, but the formation of the hydroxy acid, that is to say of the lactone, can only have resulted from ring-disrupture. As, moreover, no dialdehyde could be isolated from the products of decomposition of the crude ozonide, Semmler believes that the hydroxy acid, and also the lactone, are not formed from the cyclic-unsaturated isocamphene but also from the semicyclic camphene, which must consequently form the chief constituent of the crude camphene. Ozone did not react in any way

¹⁾ Journ. russ. phys.-chem. Ges. 40 (1908), 1015. Quoted from Chem. Zentralbl. 1908, II. 1865.

²⁾ Liebig's Annalen 245 (1888) 254.

³⁾ Berl. Berichte 42 (1909), 246.

with camphenilone or fenchone. Semmler gives the following formulæ for the separate processes: —



Terpinene. F. W. Semmler¹⁾ has made a critical study of the statements recorded relating to terpinene obtained by various different methods. He calls attention to the fact that there is a series of contradictory statements on this subject, especially as regards the exaltation which has been observed, and the formation of the nitrosite. His experiments, which are described below, point the way towards a clearing-up of this involved condition of things, but the results obtained do not even now permit of any certain conclusions to be drawn. By treating carvenone with pentachloride of phosphorus, without application of heat, Semmler obtained a monochloride of carvenene, $C_{10}H_{15}Cl$, which was converted into carvenene, $C_{10}H_{16}$, by reducing it with sodium and alcohol. This body possessed the following constants: b. p. 179,5 to 180,5° at 735 mm. press., 61 to 63° at 10 mm. press., d_{20}^0 0,844, n_D 1,491, molec. refraction, found 46,74, calculated for $C_{10}H_{16}/2$ 45,24. According to its origin, this hydrocarbon should be 4^{1,3}-dihydrocymene, and might therefore be identical with terpinene²⁾. But, in contradistinction to the observations which have been made on terpinene, carvenene showed an exaltation of about 1,5. On the other hand it gave the nitrosite reaction, although not very readily. This experiment shows that conjugated cyclic linkings may cause exaltation.

Up to the present no inversion had been observed in the treatment of terpinene with acids. But when carvenene was boiled for two

¹⁾ Berl. Berichte **41** (1908), 4474; **42** (1909), 522.

²⁾ Compare Report November 1908, 175.

which yields "Mutterzimt", *Cassia Lignea*, or Woodcassia, termed by the detail trade simply *Cassia*. The leaves of the tree are still used medicinally in the East Indies; in former years they were also met with in commerce (the narrow *Folia Malabathri*) but they are now obsolete. The leaves contain an essential oil of which we recently received a sample, which had been distilled by Mr. I. H. Burkill, of Calcutta. The oil was of a lemon-yellow colour, and had a clovelike, at the same time slightly peppery, odour. It possessed the following constants: $d_{15^\circ} 1,0257$, $\alpha_D + 16^\circ 37'$, $n_{D20^\circ} 1,52596$; phenol-content 78%, soluble in 1,2 volumes and over of 70 per cent. alcohol. The phenols consisted of eugenol (m. p. of the benzoyl compound 69°). When freed from phenols, the oil had the high optical rotation $\alpha_D + 66^\circ 40'$ and yielded a solid nitrite which, when recrystallised from ethyl acetate melted at 113 to 114° . It contained therefore d- α -phellandrene. In respect of its high eugenol content it is closely allied to the ordinary oil from Ceylon cinnamon leaves.¹

Guayava Oil. The guajava tree (*Psidium Guayava* Raddi, Myrtaceæ) is a native of tropical America and bears fleshy berries which are eaten both in the raw state and as a preserve. The leaves, when chewed, are said to be a remedy in toothache, and, according to Altan¹), contain 0,36% of an essential oil with a sp. gr. $d_{15^\circ} 1,069$ and a boiling-point of about 237° .

We have recently received an oil of guajava leaves from Santiago de Cuba, which had been obtained from the raw material to the extent of 0,2%/. It was of a lemon-yellow colour and had a faint aromatic odour. We found it to possess the following constants: $d_{15^\circ} 0,9157$, $\alpha_D - 10^\circ 5'$, $n_{D20^\circ} 1,49638$, acid no. 2,0, ester no. 6,4, soluble in about 10 volumes of 90 per cent. alcohol.

Oil of *Mentha silvestris*. An oil of *Mentha silvestris* L., prepared in Cyprus, was found to possess the following properties: $d_{15^\circ} 0,9701$, $\alpha_D + 31^\circ 30'$, $n_{D20^\circ} 1,49544$, acid no. 2,4, ester no. 20,9, ester no. after acetyl. 171,4, soluble in 3 vols. of 70% alcohol; (the diluted solution showed slight opalescence;) faintly mint-like odour; yellow colour. It is obvious that the saponification number of 171,4 after acetylation of the oil cannot in this case be indicative of the menthol content, which, judging by this factor, should have been 54,8%; for as a matter of fact the sample contained but little menthol. The mint-like odour was chiefly due to the presence of pulegone, of which the oil contained 40% (isolated with neutral sulphite of sodium). In addition to this a phenol (probably carvacrol) could be detected, from which it is to be supposed that this, also, would become esterified and

¹) L'Union Pharmaceutique 1904, 494. Through Chemist and Druggist 66 (1905), 14.

(4⁶-m-menthenol-8) was formed quantitatively. This possessed an intense odour of peppermint and terpineol, boiled at 106° at 20 mm. pressure and yielded a nitroso-chloride melting at 125°. From the latter, carvestrene dihydrochloride (m. p. 52,5°) and carvestrene dihydrobromide (m. p. 48 to 49°) were obtained by means of hydrohalogen. The cis-tetrahydro carvestrenediol, which was obtained by shaking with dilute sulphuric acid, melted at 94°. By means of magnesium methyl iodide, water could readily be separated from the dihydro isocarvestrenol, and in this process isocarvestrene (b. p. 176 to 177° at 765 mm. press.) together with a diterpene C₂₀H₃₂ (di-isocarvestrene) were formed, the latter of which boiled at from 188 to 190° under 20 mm. pressure. It is remarkable that in the case of isocarvestrene it is not only the values of the refraction, but also the fact that the hydrocarbon did not yield the carvestrene derivatives referred to, which point to the presence of conjugated double-linkings in the substance.

Cadinene. In a preliminary note, N. Lepeschkin¹⁾ reports on case of isomerism in the preparation of cadinene. Cadinene prepared by heating cadinene dihydrochloride (he does not state with what) and possessing the following constants: (b. p. 148 to 149° at 20 mm. pressure; $d_{\frac{20}{40}}^{20}$ 0,9172; n_D 1,5107; $[a]_D$ — 111,28°) was converted by prolonged heating at 180 to 200° into an isomeric compound (b. p. 145 to 148° at 20 mm. pressure; $d_{\frac{20}{40}}^{20}$ 0,9061; n_{D20} 1,5041; $[a]_D$ — 2,80°). Isomerism also occurred when the substance was heated with glacial acetic acid. For the preparation of pure cadinene, for which the constants are given as follows: b. p. 271 to 272° at ordinary press.; 149° at 20 mm. press.; $d_{\frac{20}{40}}^{20}$ 0,9183; n_{D20} 1,5073; $[a]_D$ — 110,96°, the treatment of cadinene dihydrochloride with sodium alcoholate is recommended.

Caryophyllene. By oxidising caryophyllene with permanganate E. Deussen²⁾ had previously obtained a body C₁₅H₂₂O₄, m. p. 120,5° which is certainly of a glycol like character. Deussen has recently announced³⁾ that he has isolated two acids from the products of oxidation. One of these boiled under 16 mm. pressure between 186 and 190, possessed the formula C₁₀H₁₆O₃ and proved to be a monobasic ketonic or aldehydic acid, yielding a semicarbazone melting at 186°. The second acid crystallised in coarse square columns, melting at 179,5 to 180,5°. It was a monobasic acid C₈H₈O₄, which could not be identified with any known acid. Furthermore, by carrying

¹⁾ Journ. Russ. phys.-chem. Ges. **40** (1908), 698. Quoted from Chem. Zentralbl. **1908**, II. 1354.

²⁾ Liebig's Annalen **359** (1908), 258; Report November **1908**, 178.

³⁾ Berl. Berichte **42** (1909), 376, 680.

out the oxidising process in acetone solution with strong cooling, caryophyllene yielded a compound $C_{10}H_{18}O_3$, melting at 146° , which was judged by its behaviour to be a glycol.

Alcohols.

A. Windaus¹⁾, in a paper on rendering saponin non-toxic by means of cholesterol, states that digitonin may be combined with linalool, geraniol and sabinol into a crystalline compound.

Linalool. By reducing linalool by means of nickel and hydrogen, C. J. Enklaar (as already mentioned in our last Report)²⁾ obtained 2, 6-dimethyl octane. We gather from a new paper by Enklaar³⁾ that in addition to this hydrocarbon he obtained 2, 6-dimethyl octanol-6 $(CH_3)_2 \cdot CH \cdot (CH_2)_3 \cdot C(OH)(CH_3) \cdot CH_2 \cdot CH_3$ (b. p. 88 to $88,5^\circ$ at 14 mm. press.; $d_{40}^{15^\circ}$ 0,836; n_{D15° 1,4388) which points to the accuracy of Tiemann's and Semmler's formula for linalool, viz., $(CH_3)_2 : C : CH \cdot CH_2 \cdot CH_2 \cdot C(OH)(CH_3) \cdot CH : CH_2$. By the reaction of magnesium ethyl iodide on 2-methyl heptene-2-one-6 there was formed 2, 6-dimethyl octene-2-ol-6 $(CH_3)_2 \cdot C : CH \cdot CH_2 \cdot CH_2 \cdot C(OH)(CH_3) \cdot CH_2 \cdot CH_3$ (b. p. 94 to $94,5^\circ$ at 14 mm. press.; $d_{40}^{15^\circ}$ 0,8695; n_{D15° 1,4569) which, when reduced with nickel and hydrogen also yielded 2, 6-dimethyl octane and 2, 6-dimethyl octanol-6.

Menthol. In a preliminary communication, R. H. Pickard and W. O. Littlebury⁴⁾ refer to experiments for the separation of stereoisomeric menthols by the aid of their acid phthalic, or succinic esters. Thymomenthol, a body of a low melting-point, obtained by the reduction of thymol by Sabatier's process, had already been converted by Brunel⁵⁾ by esterification and subsequent hydrolysis into an isomeride, α -thymomenthol. The latter contains three, if not all four of the theoretically possible racemic combinations. Two of these can be characterised accurately and split up into their active component parts. One of these racemic menthols melted at 25° , the acid succinic ester at 86° , and the acid phthalic ester at 131° . From the fractionated crystallisation of the cinchonine or brucine salts of the last-named, a lævorotatory isomeride was obtained which, upon saponification, yielded a menthol with the same melting-point and rotation as the natural

¹⁾ Berl. Berichte **42** (1909), 244.

²⁾ Report November 1908, 153.

³⁾ Recueil des trav. chim. des P.-B. **27** (1908), 411. Through Chem. Zentralbl. **1908**, II, 1926.

⁴⁾ Proceed. chem. Soc. **24** (1908), 217.

⁵⁾ Compt. rend. **140** (1905), 252; **141** (1905), 1245; Report April 1906, 117.

combination. The second racemic product had m. p. 48 to 50°. The acid phthalic ester (m. p. 175 to 177°) could be split up into its active component by fractionated crystallisation of the brucine salt.

For the pharmacological behaviour of menthol, see p. 115.

Terpineol. It is some time since Perkin¹⁾ prepared an inactive terpineol by treating the inactive 1-methyl Δ^1 -cyclohexene 4-carboxylic ester with magnesium methyl iodide. An optically active Δ^3 -p-menthenol-8 could likewise be obtained by the same method with the aid of inactive 1-methyl Δ^3 -cyclohexene 4-carboxylic acid, which by fractional crystallisation of the brucine and strychnine salts could easily be split up into the optically active components²⁾. Recently³⁾, an easy method has been found for the preparation of the above-named 1-methyl Δ^1 -cyclohexene 4-carboxylic acid which also admitted of being readily split up into the two optically active modifications. This method has been used by Perkin, in collaboration with K. Fisher⁴⁾, for the synthesis of the optically active terpineols. When subjected to the action of magnesium methyl iodide, the esters yielded quantitatively the corresponding active terpineols which melted at 35° precisely. The specific optical rotation was found to be $[\alpha]_D + 44,2^\circ$ and $- 46,6^\circ$, whereas other authors had found higher values for this combination⁵⁾. It was easy to obtain d- $\Delta^{3,8(9)}$ -p-menthadiene from the above mentioned d- Δ^3 -p-menthenol-8 by the action of magnesium methyl iodide by the cold process, but singularly enough a conversion of the active terpineols into the corresponding limonenes under the same conditions was impossible, because almost complete racemisation supervened. The abstraction of water by means of anhydrous oxalic acid also resulted only in almost pure dipentene.

Terpinenol. In our last Report⁶⁾ we have referred briefly to O. Wallach's synthesis of terpinenol-1, and we now extract the following particulars from the more detailed account of the process which has since appeared⁷⁾.

Δ^3 -Isopropyl cyclohexenone (b. p. 95 to 96° at 12 mm. pressure; $d_{22^\circ} 0,944$; $n_{D22^\circ} 1,4817$) was treated with magnesium methyl iodide. The resulting alcohol (b. p. 92 to 97° at 14 mm. pressure; $d_{24^\circ} 0,9210$; $n_{D24^\circ} 1,4778$; mol. refr. found 47,31, calculated 47,16) boiled at

¹⁾ Journ. chem. Soc. **85** (1904), 654; Report October **1904**, 97.

²⁾ Journ. chem. Soc. **89** (1906), 839; Report October **1906**, 107.

³⁾ Journ. chem. Soc. **93** (1908), 1417.

⁴⁾ Ibidem 1871.

⁵⁾ See Report April **1908**, 186.

⁶⁾ Report November **1908**, 180.

⁷⁾ Liebig's Annalen **362** (1908), 279.

ordinary pressure apparently a little below 215° , water being given off. In the course of this reaction, phellandrene was formed, and determined by its odour and by the nitrite-reaction. It follows from this, that a displacement of the double linking must have occurred in some phase or another possibly at as early a stage as in the Grignard reaction. But the fact that the synthetically prepared alcohol contained a high proportion of terpinenol-1 could be proved by oxidation to 1, 3, 4-trihydroxyterpane, m. p. 120 to 121° . This latter substance, when treated with hydrochloric acid, yielded, in addition to cymene, a ketone which was doubtless identical with Δ^1 -menthenone. We may further place on record the fact that the optical rotatory power of sabinene hydrate in 19.17% ethereal solution is $[\alpha]_D + 53.67^{\circ}$, while that of synthetic terpinenol-4 is $[\alpha]_D + 10.53^{\circ}$. |

Guajol. A. Gandurin¹⁾, in a preliminary communication, describes experiments relating to the sesquiterpene alcohol guajol. For the purpose of isolating the compound, guajacum-wood oil was shaken up with ether for 12 hours, the resultant pulpy mass filtered with the suction pump, again shaken with ether and recrystallised from alcohol. The guajol ($C_{15}H_{25}OH$) obtained by this process occurs in prismatic crystals; it melted at 91° and, in alcoholic solution, had the rotation $[\alpha]_{D25^{\circ}} - 25.64^{\circ}$. When the substance was rubbed in the dark with a glass-rod, a pronounced iridescence of a blueish colour ensued. A hydroxyl determination according to Tschugaeff-Zerewitinoff showed the alcohol to be monatomic, the determination of the rate of esterification disclosed its tertiary character. Dihydro-gujene ($C_{15}H_{26}$) prepared according to Semmler's process by heating with zinc-dust, showed the following constants: b. p. 122° at 11 mm. press., $d_{40}^{00} 0.9089$, $d_{40}^{25^{\circ}} 0.8914$, $n_{D20,2^{\circ}} 1.49317$, $[\alpha]_{D18,5^{\circ}} - 26.65^{\circ}$, molecular refraction determined: 66.99, calculated for a bi-cyclic hydrocarbon $C_{15}H_{26}/=66.55$. As, according to Semmler, secondary alcohols are not attacked by zinc-dust, the formation of dihydro-gujene also points to the tertiary character of guajol. For the ether $C_{15}H_{25}OCH_3$, obtained by the action of methyl iodide upon the potassium compound, the following properties were established: b. p. 141 to 143° at 9 mm. press., $d_{40}^{00} 0.9513$, $d_{40}^{25^{\circ}} 0.9332$, $n_{D18,5^{\circ}} 1.48963$, $[\alpha]_{D20^{\circ}} - 31.81^{\circ}$, mol. refr. found 72.77, calculated for a bi-cyclic ether $C_{15}H_{25}OCH_3/72.83$. Application on Tschugaeff's xanthogenate method showed that — corresponding to the behaviour of tertiary alcohols — it was impossible to isolate the methyl guajyl-xanthogenate, because it decomposed immediately into guajene. This hydrocarbon showed the follow-

¹⁾ Berl. Berichte 41 (1908), 4359.

ing constants: b. p. 124° at 11 mm. press., d_{40}^{00} 0,9133, d_{40}^{250} 0,8954, n_{D250} 1,49468, $[\alpha]_{D250}$ — 66,11 $^{\circ}$, mol. refr. determined 66,46, calculated for a bi-cyclic hydrocarbon $C_{15}H_{24}$ $\sqrt{66,28}$. The whole of these results show that guajol is a tertiary sesquiterpene alcohol with one ethylene linking.

Aldehydes.

In the action of organic acids or acid anhydrides upon aldehydes, the formation of di-esters or unsaturated acids is a well-known phenomenon. F. W. Semmler¹⁾ has now further been able to prove that aldehydes in which a labile hydrogen atom is found in an adjoining position the CHO-group, are more or less easily able to yield mono-esters when subjected to the treatment mentioned above, in which process a conversion of the aldehyde into the enolic form (i. e. into the vinylic form) is to be assumed. Thus, santalol, when oxidised with ozone, yielded saturated tricyclic eksantalol²⁾, $C_{11}H_{16}O$, which was now, after being purified by means of the bisulphite combination, found to possess the following constants: b. p. 112 to 113° at 10 mm. press., d_{200} 0,987, n_D 1,4881, α_D about $+12^{\circ}$. This eksantalol, when boiled for an hour with acetic anhydride yielded, in addition to a slight quantity of diacetate, about 80% of enol-eksantalol mono-acetate (dihydro-eksantalol acetate), $C_{10}H_{14} : CH \cdot O \cdot CO \cdot CH_3$. This combination possessed the following properties: b. p. 132 to 135° at 10 mm. press., d_{200} 1,023, n_D 1,4881, α_D — $7^{\circ}15'$. By heating with water or dilute mineral acids at 110° under pressure, this body could be split up again into the aldehyde. Reduction with sodium in alcoholic solution produced eksantalol $C_{11}H_{18}O$. Whereas even with ozone no carbon atom split off from eksantalol, which indicates the saturated character of the body, the ester yielded a tri-cyclic ketone: nor-eksantalone, $C_{10}H_{14}O$, with the following constants: b. p. 101 to 102° at 10 mm. press., d_{200} 0,988, n_D 1,485, molec. refr. found 43,51, calculated 42,92. Its oxime boiled at 142 to 144° under 10 mm. pressure, and its semicarbazone melted at 216° . The corresponding alcohol, nor-eksantalol, $C_{10}H_{16}O$, boiled (10 mm. pressure) at 116 to 118° .

Phenylacetaldehyde, which behaved entirely analogously, was found to possess the following constants: b. p. 85 to 86° und 10 mm. press., d_{200} 1,0252, n_D 1,53191, molec. refr. found 36,9, calculated for C_8H_8O $\sqrt{36,7}$. Upon boiling with acetic anhydride it yielded about 80% of enol-phenylacetaldehyde mono-acetate (phenylvinyl acetate, dihydro phenyl ethyl acetate), $C_6H_5 \cdot CH : CH \cdot O \cdot CO \cdot CH_3$: b. p. 119 to 121° at 10 mm. press., d_{200} 1,065, n_D 1,5483, molec. refr. found 48,21, calculated for $C_{10}H_{10}O_2$ $\sqrt{46,32}$. Reduction produced

¹⁾ Berl. Berichte 42 (1909), 584.

²⁾ Compare Report October 1907, 85; November 1908, 182.

phenyl ethyl alcohol; oxidation with ozone, benzaldehyde (b. p. 63 to 66° at 10 mm. press.) and benzoic acid (m. p. 121°); it was also possible to split it up into the constituent parts, phenylacetaldehyde and acetic acid. Other aldehydes, such as œnanthic aldehyde, citral, citronellal, etc. showed an analogous behaviour. The well-known formation of isopulegol acetate from citronellal afforded proof that the formation of the enol-acetate precedes the closing of the ring. The physical constants of the aldehydes and their enolic mono-acetates possess regular features which enable the constitution as determined by chemical process to be tested. Moreover, the reactions described above afford a means of breaking up aldehydes into carbonyl combinations possessing one less carbon-atom, and it is further clear that if aldehydes are present when essential oils are acetylated, the alcohol content is certain to be found too high. Semmler's studies also explain certain abnormal reactions of aldehydes, such as the frequently poor yield when aldehydes are prepared from primary alcohols by oxidation with chromic acid in acetic acid solution, and the appearance, during the process of oxidation, of oxidation products containing less carbon. In any case conversions into the vinylic forms also take place on that occasion, and the readiness of aldehydes to polymerise and condense may be traced to the same cause.

A handy process for reducing salicylic acid to salicylic aldehyde is described by H. Weil¹). When treated with sodium-amalgam at ordinary temperature in the presence of boracic acid, salicylate of sodium yielded the aldehyde, which latter was removed from the action of the reducing agent by simultaneous conversion into a sparingly soluble Schiff's base by means of an aromatic amine. The Schiff's base could then be filtered off and the aldehyde recovered from it by dilute acid.

The same problem is dealt with in a paper by C. Mettler²), who succeeded in reducing benzoate and salicylate of sodium to their corresponding aldehydes by electrolysis in the presence of boracic acid, with the aid of a mercury-electrode. In this case the aldehyde was removed from the reaction-mixture by overlaying with benzene.

Piperonal. As stated in our last Report³), Delange has substituted for Fittig-Remsen's formula for piperonal dichloride $\text{CCl}_2 : \text{O}_2 : \text{C}_6\text{H}_3$, (which had been in general use for several decades,) the formula $\text{CO} : \text{O}_2\text{C}_6\text{H}_3 \cdot \text{CHCl}_2$. While engaged in experimental control tests of the arguments brought forward by Delange in support of his view, Pauly⁴), who had used the old formula in his investig-

¹) Berl. Berichte **41** (1908), 4147; German Patent 196239.

²) Ibidem **41**48.

³) Report November 1908, 194.

⁴) Berl. Berichte **42** (1909), 417.

ations, came to the conclusion that "piperonal dichloride", from piperonal and chloride of sulphur¹⁾ is, in fact, composed in accordance with the formula expressed by Delange, and not according to the old formula, which had also been adopted by us at the time. Pauly was able to afford direct proof that when reducing "piperonal dichloride" made in accordance with the patent above referred to, and purified by him by a special process, with zinc-dust in glacial acetic acid solution at a temperature not exceeding 55 to 60°, he did not recover piperonal, but instead there of the cyclic carbonic acid ester (m. p. 34°) of methyl pyrocatechol, $\text{CO}:\text{O}_2:\text{C}_6\text{H}_3\cdot\text{CH}_3$, from which, by saponification with a 50 per cent. pyridin solution, free methyl pyrocatechol, $(\text{HO})_2\cdot\text{C}_6\text{H}_3\cdot\text{CH}_3$, was obtained. This possessed a melting point of 65°, whereas up to the present 51° has been stated. The only inference to be drawn from this result is that in the course of the action of sulphur chloride on piperonal there is formed primarily a piperonal dichloride of the old formula, but that, possibly, this body, under the formation of sulphurous intermediary compounds, is converted into the cyclical carbonate of methyl pyrocatechol dichlorinated in the side-chain. According to Pauly, the circumstance that when piperonal dichloride obtained in this manner is worked up, larger or smaller quantities of protocatechuic aldehyde carbonate are produced, affords confirmation of his theory.

In connection with Pauly's communication, Barger²⁾, points out that very soon after the publication of Delange's paper, he ranged himself on the side of that investigator³⁾ in consequence of the results obtained when acting with thionyl chloride upon combinations with the methylenedioxy-group. Barger was able to show that with thionyl chloride, piperonal at a relatively low temperature yields piperonal dichloride, from which piperonal could be regenerated with formic acid. At 180°, however, the CH_2O_2 -group was also attacked, resulting in the formation of "piperonal dichloride", $\text{CO}:\text{O}_2:\text{C}_6\text{H}_3\cdot\text{CHCl}_2$, while the excess of thionyl chloride was reduced to chloride of sulphur.

Homopiperonal. To the already known reactions for distinguishing propenyl from allyl compounds, such as the different behaviour of these compounds towards acetate of mercury⁴⁾ or towards concentrated formic acid⁵⁾, F. W. Semmler and K. Bartelt⁶⁾ have added a new one. This process deals with the action of ozone

¹⁾ German Patent 165727 of Schimmel & Co.

²⁾ Berl. Berichte 42 (1909), 763.

³⁾ Journ. chem. Soc. 93 (1908), 563, 735.

⁴⁾ Berl. Berichte 35 (1902), 2995; 36 (1903), 3575; Report April 1903, 83; April 1904, 100; April 1906, 100.

⁵⁾ Berl. Ber. 41 (1908), 2185; Report November 1908, 51.

⁶⁾ Berl. Ber. 41 (1908), 2751.

upon the combinations in question. By splitting-up with water the ozonides which are formed it is found that the propenyl compounds yield the corresponding aldehydes (isosafröl, for instance, yielding piperonal), whereas allyl compounds give the corresponding homologous combinations. For example: safröl yielded, besides homopiperonylic acid, a considerable proportion of homopiperonal possessing the following properties: m. p. 69° , b. p. 143 to 144° under 10 mm. pressure, d_{20}° 1,295, n_D 1,57117, mol. refr. found 41,67, calculated 41,69. The semicarbazone melted at 189° , the oxime (b. p. 180 to 181° at 10 mm. pressure; m. p. 124 to 125°) yielded upon boiling with acetic anhydride homopiperonylic acid nitrile (b. p. 153 to 156° at 10 mm. pressure; d_{20}° 1,231; n_D 1,53698) from which by saponification homopiperonylic acid, $C_9H_8O_4$ (m. p. 127°), was obtained. The methyl ester (b. p. 153 to 155° at 10 mm. pressure; d_{20}° 1,246; n_D 1,534; mol. refr. 47,73, calculated 47,98) when reduced with sodium in alcoholic solution, yielded homopiperonyl alcohol $C_9H_{10}O_3$ (b. p. 156° at 10 mm. press. n_D 1,54780) with an odour reminding of ylang-ylang. When the nitrile referred to above was reduced, a base $C_9H_{11}O_2N$ (b. p. 146 to 148° at 10 mm. press; d_{20}° 1,225; n_D 1,5620) was formed of which the picrate melted at 160° .

Lævulic aldehyde. Lævulic aldehyde obtained by action of ozone upon unsaturated compounds such as allylacetone, methyl heptenone, 2,6-dimethyl heptadiene-2,5, citral, geraniol, linalool, caoutchouc, and gutta percha has been more closely examined by C. Harries and M. Boegemann¹). We will only briefly mention here that a series of experiments pointed to the probability of the compound possessing the formula $CH_3 \cdot CO \cdot CH_2 \cdot CH_2 \cdot CHO$, but in a few cases it behaved abnormally, which was probably due to steric conditions.

Ketones.

Sabina ketone. In continuation of previous syntheses carried out by means of sabina ketone, O. Wallach²) has now prepared some symmetrical di-isopropyl derivatives. He condensed sabina ketone with isopropyl magnesium iodide, and by decomposing the resulting product, he obtained an alcohol with an odour reminding of terpeneol, and a b. p. of 102 to 107° at 14 mm. pressure. When shaken with dilute sulphuric acid this alcohol was slowly converted into the corresponding terpene:



¹) Berl. Berichte 42 (1909), 439.

²) Liebig's Annalen 362 (1908), 283.

m. p. 139° . By treating it with hydrohalogen he also succeeded in preparing the di-hydrochloride (m. p. 111 to 112°) and the di-hydrobromide (m. p. 120 to 121°).

Menthone. We desire to give some further particulars of a paper by O. Wallach¹⁾ to which reference has already been made in our last Report²⁾. A synthesis of i-menthone was carried out in the following manner. By condensing 1,4-methyl cyclohexanone with bromo-isobutyric ester and further treating the product by the method frequently described, a hydrocarbon $\text{CH}_3 - \text{C}_6\text{H}_{10} = \text{C} = \text{C}(\text{CH}_3)_2$ was prepared and inverted into i-menthene³⁾. The i-menthene obtained therefrom by means of its nitroso-chloride was then reduced to i-menthol and from this i-menthol was obtained i-menthone by oxidation. The semicarbazone of this compound melted at 210 to 212° , the oxime at 77 to 79° . Hereby its identity with i-menthone obtained from 1,3,4-trihydroxyterpane in the sequence of reactions already described, was demonstrated.

Further, by brominating Δ^4 -menthene, a dibromide (m. p. 36°) was obtained, while reduction yielded a not entirely congealing menthol which obviously contained a mixture of stereoisomeric menthols. The presence of i-menthol could be proved by oxidising the substance to a ketone, from the semicarbazone of which portions of 210 to 212° m. p. could be isolated. Up to the present nothing has yet been determined as to the nature of those fractions of the semicarbazone which have a lower melting point.

E. Beckmann⁴⁾, has continued, in collaboration with E. Müller his researches into the optically active menthones, to which we briefly referred at the time⁵⁾. It is known that l-menthone, $[\alpha]_D - 28,5^{\circ}$, which had been previously obtained from natural l-menthol by oxidation with chromic acid mixture, could be converted with cold 90% sulphuric acid into a dextrorotatory isomer, $[\alpha]_D + 28,1^{\circ}$. The original surmise that notwithstanding the equal degree of rotation, this case was not one of a simple optical antipode of the original ketone, was confirmed in the sequel by the isolation of a strongly dextrorotatory ketone, d-isomenthone, from the mixture with unaltered l-menthone. From a mixture of several isomeric mentholes which occur in the process of reducing l-menthone or inverted d-menthone, a d-isomenthol (m. p. 78 to 81° ; $[\alpha]_D + 2,03^{\circ}$) was also obtainable and from this, again, d-isomenthone, $[\alpha]_D$ up to $+ 35,1^{\circ}$. Reduction of the oximes

¹⁾ Liebig's Annalen **362** (1908), 261.

²⁾ Report November **1908**, 180.

³⁾ Report October **1906**, 114.

⁴⁾ Berl. Berichte **42** (1909), 846.

⁵⁾ Report April **1904**, 116.

of the separate menthones into the menthylamines, and the conversion of the latter by means of nitrous acid, resulted in derivatives of still higher rotating-power; thus, from the lævorotatory total product there was obtained a d-isomenthol, $[\alpha]_D + 25,6^\circ$, and, further, from such a body with $[\alpha]_D + 26,3^\circ$, m. p. 83° , there was prepared an isomenthone with the high specific rotation $[\alpha]_D + 93,2^\circ$.

That inverted d-menthone is made up of several isomers has also been shown recently by the investigation of the oximes. Whereas l-menthone oxime melts at 59° , the oxime of inverted d-menthone appears as a viscous oil, which, however, like the oxime of the former, yields a crystalline hydrochlorate. The solid hydrochloride, which was separated out from a solution of inverted d-menthone in absolute ether by the introduction of relatively little dry hydrogen chloride, possessed when purified, a melting point of 132° , (it turned brown), and a sp. rot. $[\alpha]_D + 35,9^\circ$. Hydrochloric acid being again introduced into the filtrate of these crystals, there separated out another hydrochloride, at first of a viscous consistency, but solidifying when dried *in vacuo* over soda-lime. This hydrochloride had $[\alpha]_D - 62,6^\circ$, and melted at 117 to 118° (turning brown in the process). It corresponds to the oxime-hydrochloride of true l-menthone, while the hydrochloride which was first separated is identical with the corresponding derivative of d-isomenthone.

The oximes which were liberated from the hydrochlorides by means of sodium carbonate possessed the following characteristics: the viscous oxime of inverted d-menthone had $[\alpha]_D - 6^\circ$; the oxime of l-menthone melted at 59° , and had $[\alpha]_D - 42,5^\circ$; the oxime of d-isomenthone was again viscous and had $[\alpha]_D + 41,0^\circ$. The pure ketones forming the bases of the oximes could not be recovered unaltered from the latter, on account of the inversion which ensued during the splitting-up process, but after the foregoing there was no doubt that inverted d-menthone consists of a mixture of l-menthone and d-isomenthone.

Experiments previously made to separate the ketones over the semicarbazones were repeated and then led to the following results: inverted d-menthone yielded a semicarbazone, m. p. 116° , and with a specific rotation, in aqueous solution of chloral hydrate, $[\alpha]_D + 26,6^\circ$, the semicarbazone from d-isomenthone had a melting point of 154° and $[\alpha]_D + 46,5^\circ$, and the derivative of l-menthone, m. p. 184 , which had already been prepared before, had a specific rotation of -64° .

Pulegomenthone which was previously obtained from pulegone hydrobromide could not be split up by similar treatment of its oxime with hydrochloric acid.

Beckmann finally announces that he intends to publish elsewhere a detailed report on this and allied investigations.

Camphor. Further detailed particulars concerning the total synthesis of racemic camphor, which was first carried out by G. Komppa several years ago are now available¹⁾. Long ago the researches of Haller²⁾, and of Bredt and v. Rosenberg³⁾, had described a process for the conversion of active camphoric acid into active camphor, but the problem still remained of converting Komppa's synthetic racemic camphoric acid⁴⁾, by this process, into camphor. For this purpose the acid (m. p. 202 to 203°; $\alpha_D \pm 0^\circ$) was converted into campholide by the reduction of its anhydride (m. p. 220 to 220,5°). This campholide melted at 211,5 to 212° and yielded bromocampholic acid (m. p. 178 to 179°). The cyanocampholic acid obtained by heating of campholide with potassium cyanide was saponified to the corresponding homocamphoric acid (m. p. 231 to 232°), the calcium salt of which, when subjected to dry distillation, was converted into racemic camphor with a m. p. of 178 to 178,5°, this melting point not being reduced when the substance was mixed with a preparation obtained by combination of d- and l-camphor. The oxime melted at 118°. Komppa has also projected a total synthesis of active camphor by the splitting-up of racemic camphoric acid into its active components by the aid of quinine, (by which process it has already been possible to produce pure l-camphoric acid,) or by splitting-up camphor itself over the corresponding borneols.

Induced by this communication, E. Beckmann⁵⁾, has published the result of experiments which were made by him, jointly with E. Saran, as far back as in 1897. Isoborneol prepared by us from camphene by Bertram's and Walbaum's process, only possessed a rotation of a few degrees and consisted chiefly of a racemic mixture, for the derivatives obtained from it (camphor m. p. 177°, camphoric acid m. p. 200 to 202°, camphoric anhydride m. p. 219 to 220°,) also rotated but very feebly. For separation into the optically active component parts, the acid cinchonidine salt of camphoric acid melting at 196 to 198°, was employed. By fractionated crystallisation, dextro and lævorotatory camphoric acid, (m. p. 183°; $[\alpha]_D +44,4^\circ$; and m. p. 186 to 187°, $[\alpha]_D -50,7^\circ$ respectively) were obtained from this. Besides the above, experiments were tried of separating the isoborneol itself by fractional crystallisation of the cinchonidine salt (m. p. 107°) of its acid succinate, but this process of decomposition was only partly carried out. Afterwards, Pickard and Littlebury succeeded in completely decomposing isoborneol by an analogous process, with regard to which we made a communication at the time⁶⁾.

¹⁾ Berl. Berichte **41** (1908), 4470.

²⁾ Compt. rend. **122** (1896), 446; **130** (1900), 376.

³⁾ Liebig's Annalen **289** (1896), 1.

⁴⁾ Berl. Berichte **36** (1903), 4332; Report April **1904**, 98.

⁵⁾ Berl. Berichte **42** (1909), 485.

⁶⁾ Comp. Report April **1908**, 185.

Isopulegone. The treatment of isopulegone with magnesium methyl iodide and the conversion of the resulting 3-methyl isopulegol into 3-methyl $\Delta^{2,8(9)}$ -menthadiene, to which reference has already been made in our last Report¹⁾, has been the subject of a detailed paper by A. Ebert²⁾. For particulars as to constants, as well as for details concerning the mode of the splitting-off of water (which was carried out according to various methods), we refer to the original paper.

Umbellulone. F. W. Semmler³⁾ has recently entered the lists once more in the controversy which is being carried on between Tutin and himself on the constitution of umbellulone; his object on this occasion being to controvert Tutin's objections, which were discussed in our recent Reports⁴⁾. Tutin having maintained that Semmler's arguments referred in reality to a foreign body which was mixed with the umbellulone, the latter repeated his experiments, using for that purpose an umbellulone which had been regenerated from the semicarbazide compound. Umbellulone, obtained by fractionating an oil distilled by us, was found to possess the following constants: b. p. 92 to 94° at 10 mm. press., $d_{20} 0,950$, $n_D 1,4872$, $a_D - 37^\circ 30'$. In addition to the semicarbazide-semicarbazone which had already been described by another investigator (and which Semmler now showed to possess a m. p. above 200°), the author was also able to prepare the normal mono-semicarbazone with a m. p. between 240 and 243°. The umbellulone regenerated from the last-named product by decomposition with dilute sulphuric acid gave the following constants: b. p. 92,5 to 93° at 10 mm. press., $d_{20} 0,950$, $n_D 1,48325$, $a_D - 36^\circ 30'$. The preparation obtained from the semicarbazide-semicarbazone showed the following constants: b. p. 92 to 94° at 10 mm. press., $n_D 1,4825$, $a_D - 37^\circ$. For β -dihydro umbellulol obtained from the regenerated umbellulone the following constants were determined: b. p. 88 to 92° at 10 mm. press., $d_{20} 0,927$, $n_D 1,4696$, $a_D - 27^\circ 45'$; for β -dihydro-umbellulone: b. p. 84 to 86° at 10 mm. press., $d_{20} 0,925$, $n_D 1,4616$, $a_D - 30^\circ$. The benzylidene-compound prepared from the last-named, when oxidised with permanganate in acetone solution, yielded (as before) homotanacetone dicarboxylic acid (m. p. 147°). Hence the assertion of Tutin, that Semmler's benzylidene compound was not derived from β -dihydro-umbellulone, falls to the ground. Without doubt the quantitative conversion into thymol (m. p. 52°, b. p. 111° at 10 mm. press., $d_{20} 0,977$, $n_D 1,52148$, $a_D \pm 0^\circ$) by prolonged heating

¹⁾ Report November 1908, 186.

²⁾ Zeitschr. d. allg. oesterr. Apoth. Ver. 46 (1908), 545, 561, 573, 589.

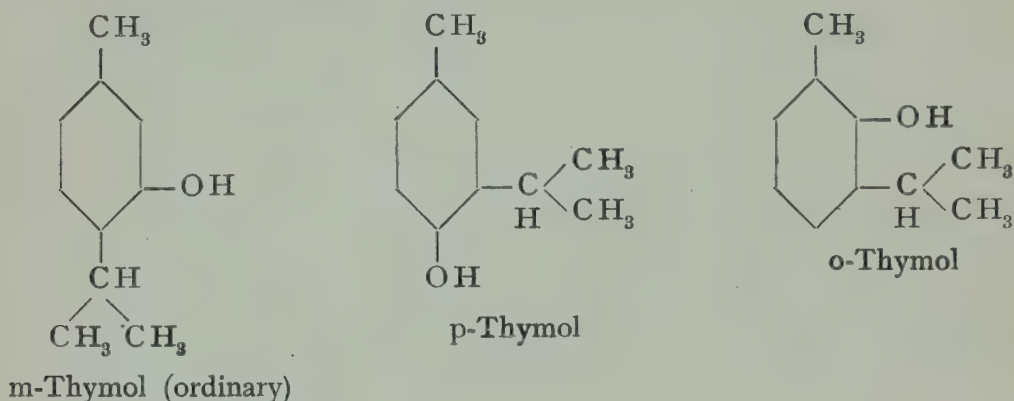
³⁾ Berl. Berichte 41 (1908), 3988.

⁴⁾ Report April 1908, 108; November 1908, 126.

of umbellulone in a sealed tube, which has now been carried out by Semmler, is evidence of the correctness of that investigator's statement as to the constitution of umbellulone.

Phenols and Phenol-Ethers.

In his dissertation¹⁾, of which a copy was courteously sent to us, C. Guillaumin describes ortho and parathymol.



For the preparation of para-thymol, para-thymol methyl ether (prepared from pseudo-allylcresol methyl ether and sodium in alcoholic solution), was treated in acetic acid solution according to Störmer's method with hydrobromic acid. Ortho-thymol is prepared in precisely the same manner.

Para-thymol occurs in long, colourless needles, m. p. 36° , b. p. 228 to 229° (corr., at 760 mm. press.), $d_{0^{\circ}} 0,9954$, $d_{17,8^{\circ}} 0,9817$, $n_{D17,8^{\circ}} 1,52438$. The odour of para-thymol is less pronounced than that of ordinary thymol, and reminds of para-cresol.

Ortho-thymol was not obtained in crystalline form; it appears as a colourless liquid, b. p. 225 to 226° (corr., at 760 mm. press.), $d_{0^{\circ}} 0,9986$, $d_{15,2^{\circ}} 0,9865$, $n_{D15,2^{\circ}} 1,52385$.

After giving a list of the literature existing on the pharmacological behaviour of thymol, the author compares this behaviour with that of the new isomers.

With regard to toxicity, experiments on rabbits gave the following results: —

The fatal dose per kilo rabbit was: —

$0,033$ g. for ordinary thymol;
 $0,036$ g. for p-thymol;
 $0,045$ g. for o-thymol.

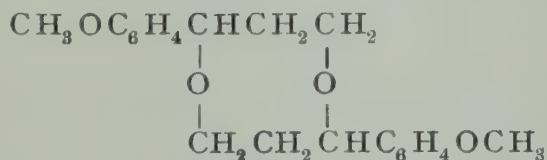
¹⁾ C. Guillaumin, *Étude chimique et pharmacologique des thymols synthétiques dérivés des acides crésotiniques*. Paris 1909.

As regards antiseptic action, para-thymol does not appear to be inferior to the natural product, but ortho-thymol is only half as effective.

In order to form an opinion as to the possibility of employing thymol as a remedy for intestinal worms, the author has experimented with such worms (*anchylostomum*), but here also he found ordinary thymol to be superior to its isomers, while ortho-thymol had the least powerful effect.

In respect to therapeutic efficiency the natural product appears from this to be superior to both isomers.

L. Balbiano¹⁾, by treating anethol with acetate of mercury, had prepared two glycols of anethol from which, by dehydration, he obtained a hydrocinnamic aldehyde. On the other hand, Tiffeneau and Daufresne²⁾ alleged that by treating one of the glycols with 20% sulphuric acid they obtained anise ketone. Balbiano now, in a fresh paper³⁾, declares that, contrary to the experience of Tiffeneau and Daufresne, he obtained by an experiment carried out in the same way, from both glycols (the α -glycol, m. p. 62 to 63° and the β -glycol, m. p. 114 to 115°) the same p-methoxy hydrocinnamic aldehyde (b. p. 136 to 137° at 10 mm. press.; semicarbazone, m. p. 175 to 176°). In addition there was formed a small quantity of a compound (m. p. 181 to 182°) to which, from its behaviour, the following formula is assigned: —



For details, we refer to the original paper.

With regard to the occurrence of 1-allyl-2, 3, 4, 5-tetramethoxybenzene in French oil of parsley, see p. 73.

Acids.

The ketone $\text{C}_7\text{H}_{10}\text{O}$ ⁴⁾ which was obtained by Wallach by the oxidation of Δ^1 -cyclohexene acetic acid or Δ^1 -methylcyclohexene and which, upon further oxidation, yielded glutaric acid, the nature of which,

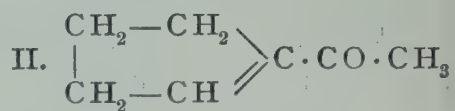
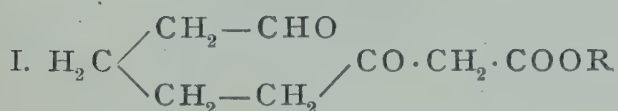
¹⁾ Comp. Report April 1906, 99.

²⁾ Compt. rend. **144** (1907), 1354; Report October 1907, 169.

³⁾ Rendiconti della R. Acc. dei Lincei **17** (1908), 259. We quote from a copy kindly sent to us.

⁴⁾ Liebig's Annalen **343** (1905), 53; **353** (1907), 292; **359** (1908), 308 Report April 1906, 128; October 1907, 177; November 1908, 197.

however, had to be determined still, has now been recognized as Δ^1 -acetylcycl opentene. This statement has been made in a joint paper by O. Wallach and W. H. Perkin jun.¹⁾ Perkin, when oxidising the ethyl ester of the Δ^1 -cyclohexene acetic acid with ozone²⁾, had obtained an aldehydo ketonic ester (I) which, when boiled with sulphuric acid, was converted into Δ^1 -acetyl cyclopentene (II) which could be identified with the ketone $C_7H_{10}O$ obtained from the acid itself.



By condensing cyclopentanone with bromo-propionic ester according to the series of reactions generally used for the preparation of tetrahydrated extracyclic ring ketones³⁾, Wallach had also succeeded in producing Δ^1 -acetyl cyclopentene and had also recognized its identity with the ketone obtained from cyclohexene acetic acid, because the derivatives of the two ketones possessed the same properties (oxime m. p. 90 to 91°, benzoyl oxime m. p. 116 to 117°; semicarbazone m. p. 203 to 204°). According to Perkin's experiments it is to be assumed that Δ^1 -cyclohexene acetic acid produces in the first place a ketonic aldehyde which is immediately converted, by internal condensation, into acetyl cyclopentene. Such an unlooked-for result of an oxidation with permanganate shows the extreme caution which must be exercised in forming theories regarding the constitution of a body from oxidative analysis.

Cinnamic acid. With regard to the complicated isomerism of the different cinnamic acids, new and far-reaching researches have been published, the main features of which we will briefly pass in review.

E. Erlenmeyer jun.⁴⁾ has made investigations into the problem as to what is the origin of the difference between synthetic cinnamic acid and natural cinnamic acid from storax. The two acids differ, for instance, in the manner in which they crystallise from ether, as well as in regard to solubility. The synthetic acid melts at 132 to 133°, the acid from storax at 134 to 135°. It was shown that synthetic cinnamic acid is a uniformly crystallising mixture made up of about equal parts of storax- α -acid and an isomeric combination termed hetero- α -cinnamic acid. It is very difficult to split up the mixture by crystallisation, as the two component parts evidently exert mutual molecular attraction. No admixture of other products could be detected.

¹⁾ Berl. Berichte 42 (1909), 145.

²⁾ Journ. chem. Soc. 93 (1908), 1946.

³⁾ Report November 1908, 166.

⁴⁾ Berl. Berichte 42 (1909), 502.

In order to separate the synthetic cinnamic acid into its component parts, the ethyl ester was subjected to careful fractional distillation *in vacuo*. After saponification there was obtained, from the fractions with the lowest boiling points, storax cinnamic acid, and from those with the highest boiling points and from the residue the combination formerly¹⁾ described as "new triclinic cinnamic acid", and now as "hetero-cinnamic acid". This combination, like the storax acid, can occur either in the α or the β -form, and the two forms can be both converted into each other. The acid recovered from the residue by the method of separation above indicated was the β -form. It occurred as a lustreless, light, chalky powder; m. p. 128° . It was more readily soluble in water, ether, alcohol, or ligroin than were either the storax acid or the synthetic acid. The acid was easily convertible into the α -form, which separated out in lustrous, small crystalline flakes, but the hetero- β -cinnamic acid was less inclined to conversion than was the storax- β -acid, and it was therefore generally very easy to re-convert the hetero- α -cinnamic acid into the β -acid. The m. p. of the hetero- α -acid was 130 to 131° . In the method of separation by the aid of the esters, as set forth above, the β -acid was formed from the α -acid by conversion, because the synthetic cinnamic acid was obtainable in its characteristic crystalline form by combination of hetero- α -cinnamic acid and storax- α -cinnamic acid after crystallisation from ether, whereby the proof of its composition was given. The two acids formed mixed crystals in every proportion; but on the other hand, when hetero- β -cinnamic acid and storax- α -acid were dissolved together, the former was partly converted into hetero- α -acid, so that crystallisations of altogether different characteristics were obtainable. No uniform mixed crystals were observed in this case.

A further paper²⁾, connecting with that abstracted above, discusses the differences in chemical behaviour of the isomeric acids obtained from synthetic cinnamic acid as regards the formation of salts and the additive reactions. Without entering into details, we will only mention, that besides salts which showed great exterior resemblance, others were obtained which presented marked differences. In the matter of additive reactions, the two acids distinguished themselves by considerable divergence in the rate of speed of the reactions. By means of fractionated precipitation of the sodium salt with hydrochloric acid it was furthermore possible, owing to the difference in strength of the two acids, to devise a process for splitting-up the synthetic acid into its two component parts. Worthy of note also is the property possessed by storax acid, synthetic cinnamic acid and hetero- β -acid, as mono-basic acids, of yielding acid salts which must be derived from double

¹⁾ Report April 1907, 156.

²⁾ Berl. Berichte 42 (1909), 182.

molecules. But as regards this property, analogous behaviour has been observed in other cases, for instance in that of benzoic acid. In fact, the ability of giving double molecular reactions appears to be more frequent generally than could have been expected up to the present. Erlenmeyer attributes the isomerism observed in the cinnamic acids to the power possessed by the benzene nucleus of existing in several more or less stable conditions which, in the case of the cinnamic acids, are distinguished by special stability. Thus it was possible to obtain the benzaldehydes corresponding to the two cinnamic acids; but particulars as to this part of the investigations are deferred to a subsequent communication.

Shortly before the appearance of the above-mentioned work of Erlenmeyer, a paper by E. Biilmann¹⁾ had appeared, which seemed to give a surprisingly simple solution of the problems of isomerism which exist in the chemistry of cinnamic acids. In this paper no speculations with regard to new varieties of isomerism were propounded. In Biilmann's opinion, allo-cinnamic acid (m. p. 68°) and the two isocinnamic acids with respective melting points of about 57° and 38 to 46° , are not isomeric, but are chemically identical bodies, in which the only question at issue is one of simple trimorphy. Provided certain exceptional measures of precaution were observed, each of the three acids could be converted quantitatively in the time of a few seconds into any of the others, by melting it and inoculating the molten substance, when cooled, with the desired variety. Thus a plausible explanation might be found for the origination of the separate forms. But Erlenmeyer²⁾ points out that Biilmann's observations are not quite sufficient to disprove the theory that the three cinnamic acids present exceedingly labile, mutually inter-convertible isomers. The assumption of simple polymorphy would not be consonant with several of the facts observed, and further investigations are therefore considered necessary before a definite opinion can be formed.

Nitrogenous Bodies.

From a paper by F. Wechuizen³⁾ we abstract the following data, referring to the detection of indol in flowers. If the available quantity of flowers is large enough to admit of the preparation of essential oil, the presence of indol may be proved by means of the crystalline combinations which it gives with sodium bisulphite and picric acid. In other cases the method given by Verschaffelt⁴⁾ may be applied,

¹⁾ Ibidem 513.

²⁾ Ibidem 521.

³⁾ Pharm. Weekblad 45 (1908), 1325. From a copy kindly sent to us.

⁴⁾ Report October 1905, 123.

in which the odour exhaled by the flowers is allowed to act upon oxalic acid. Weehuizen has now successfully tested the practicability of the colour reactions for indol indicated by Steensma¹⁾ for showing the presence of this combination in the scent of flowers. The crushed flowers were extracted with alcohol for about 5 minutes, and a little vanillin or p-dimethylamino benzaldehyde was dissolved into the filtrate, whereupon after the addition of a few drops of concentrated hydrochloric acid the characteristic red colorations ensued. When p-dimethylamino benzaldehyde was employed, the reaction could be made still plainer by the addition of a trace of sodium nitrite. As phloroglucinol gives the same colour reactions, another process, which may be followed when this combination is present, is that of exposing filtering paper or spun glass soaked in a 1% solution of vanillin or p-dimethylamino benzaldehyde in a mixture of equal volumes of alcohol and concentrated hydrochloric acid, for a long time to the exhalations of the flowers. When dried at ordinary temperature a red coloration will then take place. The last-named process is also to be applied when the alcoholic extracts of the flowers are coloured.

In this manner the presence of indol could be shown in the white flowers of *Murraya exotica* L. (*Murraya sumatrana* Roxb.) and in the spadices of one of the numerous varieties of *Caladium* with variegated leaves.

¹⁾ Zeitschr. f. physiol. Chem. 47 (1906), 25.

Solubility Table of the Most Used Odoriferous Substances

100 parts by weight of solvent dissolve at 10° C.	96 p. c. Alcohol	70 p. c. Alcohol	Glycerine	Olive oil	Paraffin
Anethol	20	3	s. l. ¹⁾	10	6
Anisic aldehyde (Aubépine)	∞ ²⁾	130	0,1	∞	1,5 (op)
Benzaldehyde	∞	70	0,1	∞	7
Benzoic acid ethyl ester .	∞	45	s. l.	∞	∞
Benzoic acid methyl ester	∞	65	0,1	∞	∞
Benzyl acetate	∞	50	0,1	∞	13
Benzyl alcohol	∞	∞	∞	∞	1
Benzyl benzoate	∞	3	s. l.	∞	18
Bornyl acetate	∞	30	s. l.	∞	∞
Cassia oil, artificial, Sch. & Co. (see cinnamic aldehyde).					
Cinnamic aldehyde	∞	30	0,1	∞	1,5 (op)
Cinnamic alcohol	∞	∞	1	11	0
Cinnamic acid benzyl ester	∞	1,5 (cloudy)	s. l.	∞	4 (opa)
Cinnamic acid ethyl ester	∞	13	s. l.	∞	∞
Cinnamic acid methyl ester	∞	50	s. l.	∞	∞
Cinnameïn (see Peru bal- sam oil).					
Citral	∞	40	s. l.	∞	∞
Citronellal	∞	25	s. l.	∞	∞ (op)
Citronellol	∞	55	0,1	∞	∞
Coumarin ³⁾	8	4	0,1	1,5	0
Eucalyptol	∞	55	0,1	∞	∞
Eugenol	∞	110	0,1	∞	3 (opa)
Geraniol	∞	65	0,1	∞	∞
Geranyl acetate	∞	6 (cloudy)	s. l.	∞	∞

¹⁾ s. l. = solubility less than 0,1:100.

²⁾ ∞ = soluble in any proportion.

³⁾ For details as to the solubility of coumarin in alcohol, see Report April 1899,

parts by weight of solvent dissolve at 10° C.	96 p. c. Alcohol	70 p. c. Alcohol	Glycerine	Olive oil	Paraffin oil
ranyl methyl ether . .	∞	6 (opal.)	s. l.	∞	∞
liotropin (Piperonal) .	8	5	s. l.	6	0,8 (opal.)
acanth, Sch. & Co. . .	∞ (opal.)	3 (opal.)	s. l.	∞	2 (opal.)
eugenol	∞	115	0,1	∞	0,7 (opal.)
safrol	∞	2	s. l.	∞	∞
mine, Sch. & Co. . .	∞	150	0,1	∞	2
ac, Sch. & Co. . . .	∞	65	0,1	∞	∞
y of the Valley, Sch. & Co.	∞	100	0,1	∞	4
alool	∞	50	0,1	∞	∞
alyl acetate (Bergamiol)	∞	24	0,1	∞	∞
nthol	300	23	0,1	10	10
thylanthranilic acid me- thyl ester	∞	7	s. l.	∞	∞
sk, artificial, Sch. & Co. ¹⁾	0,5	s. l.	s. l.	2,5	0,7
sk, artificial, Sch. & Co., extra soluble	1,1	0,2	s. l.	2,5	0,7
sk-seed (Ambrette) oil, Sch. & Co.	∞	2	s. l.	∞	∞
guet (see Lily of the Valley).					
rcissus, Sch. & Co. . .	∞	95	0,1	∞	∞
oviolone 100%	∞	40	s. l.	∞	∞
roli, Sch. & Co. . . .	∞	35	s. l.	∞	∞
rolin I	5	0,8	s. l.	13	6
rolin II	2	0,4	s. l.	3	2
obe oil (see Benzoic acid methyl ester).					
oviol	∞	25	s. l.	∞	∞
ris oil, liquid, Sch. & Co.	∞	6	s. l.	∞	∞
ris oil, solid	10	s. l.	s. l.	2	0,8
racresol methyl ether :	∞	10	0,1	∞	∞
ru balsam oil	∞	1,5 (opal.)	s. l.	∞ (opal.)	0,7 (opal.)
enyl ethyl alcohol . .	∞	∞	1,5	∞	1,5

¹⁾ For solvents for artificial musk, see also Bericht April 1905, 123.

100 parts by weight of solvent dissolve at 10° C.	96 p. c. Alcohol	70 p. c. Alcohol	Glycerine	Olive oil	Paraffin oil
Pink blossom oil, Sch. & Co.	∞	80	0,1	∞	1,5 (opal.)
Reseda-Geraniol, Sch. & Co.	∞	50	0,1	∞	∞ (opal.)
Rose oil, artificial, Sch. & Co.	20 ¹⁾	20 ¹⁾	s. l.	50	50
Rose oil, artificial, liquid, Sch. & Co.	∞	30 ²⁾	s. l.	∞	∞
Rose oil, natural, free from stearoptene	∞	30	s. l.	∞	∞
Safrol	∞	3	s. l.	∞	∞
Salicylic acid amyl ester .	∞	1	s. l.	∞	∞
Salicylic acid ethyl ester .	∞	7	s. l.	∞	∞
Salicylic acid methyl ester	∞	11	0,1	∞	∞
Santalol	∞	25	0,1	∞	∞
Terpineol, liquid	∞	60	0,1	∞	∞
Thymene	∞	1	s. l.	∞	∞
Thymol	200	30	0,1	50	5
Tréfol (see Salicylic acid amyl ester).					
Vanillin	38	30	1	0,9	s. l.
Wallflower, Sch. & Co. .	∞	∞	0,1	∞	0,4 (opal.)
Wintergreen oil, artificial (see Salicylic acid methyl ester).					
Ylang-Ylang, Sch. & Co. .	∞	40	s. l.	∞	∞

¹⁾ Soluble with strong separation of paraffin; completely soluble only when greatly diluted.

²⁾ Soluble with slight separation of paraffin; completely soluble only when greatly diluted.

Examination of the Essential Oil
of
Blumea balsamifera D. C.

By

Richard Jonas

of Brussels.

Blumea balsamifera, a shrub-like plant of the family of the *Compositae*, is a native of India, and occurs from the Himalayas down to Singapore and the Malay Archipelago. According to recent reports it also flourishes abundantly in Tonquin¹). The product of distillation of the plant is solid and consists of the so-called "Ngai-camphor", with which only very little liquid oil is found admixed. This Ngai-camphor (*Ngai-fên*) is used by the natives of the countries aforementioned for medicinal purposes and in religious rites, as well as in the preparation of Indian ink. It was first recognized as l-borneol by Plowman²), Flückiger³), and Haller⁴). With this exception nothing was known up to the present as to the chemical composition of true Ngai-camphor oil. A number of years ago, Schimmel & Co. came into possession of a dark-brown oil, possessing a characteristic odour reminding of borneol, but probably this oil had already been freed from the bulk of its borneol by distillation with water vapour.

This oil possessed the following properties: $d_{15^{\circ}} 0,950$, $a_D - 12^{\circ} 30'$, $n_{D20^{\circ}} 1,48151$, acid no. 23,35, ester no. 1, ester no. after acetylation 198 (corresponding to 63,95% of alcohol $C_{10}H_{18}O$). Fractional distillation under reduced pressure yielded a first fraction of 6,3 g. of an oil with b. p. 38° (40 mm. press.) to 80° (30 mm. press.). In this, as well as in the next fraction, cineol could be identified by the iodol compound m. p. $111,5^{\circ}$. The next following fraction ($a_D + 4^{\circ} 10'$) which distilled between 80° (30 mm. press.) and 75° (12 mm. press.) gave a nitroso chloride with a m. p. of $103,5^{\circ}$. Taking into account the boiling point of this fraction it is probable that the nitrosochloride was that of limonene. As the further progress of distillation *in vacuo* was made difficult through the liberal separation of solid crystals (borneol) it became necessary to remove this substance by freezing it out. But before this was done the oil was first treated with dilute sodium carbonate solution and subsequently with a 5% soda liquor. With the latter, a phenol-like body was isolated from the oil, to which detailed reference shall be made below. The sodium carbonate solution dissolved traces of two solid acids, probably palmitic acid and myristic acid. The crystals which separated under strong cooling from the phenol-and-acid-free oil consisted of a mixture of l-borneol and l-camphor. In order to isolate the borneol, part of this mixture

¹) Journ. d'Agriculture tropicale 8 (1908), 30; Report April 1908, 150.

²) Pharmaceutical Journal III. 4 (1874), 710; Neues Repert. f. d. Pharm. 23 (1874), 325.

³) Pharmaceutical Journal III. 4 (1874), 829.

⁴) Bericht October 1889, 54.

was heated for 6 hours to 110° with phthalic anhydride in an autoclave; the resulting acid phthalic ester dissolved in dilute sodium carbonate solution, and the alkaline solution after having been repeatedly extracted with ether, distilled in a steam current with addition of soda liquor. The borneol, which volatilised readily with water vapour, congealed in the receiver in the shape of leaf-like crystals with m. p. of 203° . The distillation residue of the ether solution, when treated with hydroxylamine, yielded camphoroxime, m. p. 118 to 119° . The residual oil, freed from borneol and camphor, consisted mainly of a mixture of sesquiterpenes and sesquiterpene alcohols, which, after distillation in a current of steam, boiled at about 280° .

A special interest attaches to the phenol which had been extracted from the oil by the soda liquor. It is precipitated from the alkaline solution, when acid is added thereto, in the form of a yellowish, solid body which becomes colourless after repeated re-crystallisation from benzene and petroleum ether, and melts at 82 to 83° . It is soluble in the other organic solvents. With ferric chloride it assumes a deep red colour. An elementary analysis of the phenol pointed to the formula $C_{10}H_{12}O_4$.

	Found:			Calculated for $C_{10}H_{12}O_4$:
	I	II	III	
C	60,50%	60,99%	60,75%	61,22%
H	5,85%	6,04%	6,17%	6,12%

The molecular weight determined according to Beckmann (in benzene solution) was found to be 212 (theory 196) and corresponds to the formula above. Methoxyl determinations in Zeisel's apparatus established the fact that the phenol contained two methoxyl groups: —

1. 0,3264 g. subst.: 0,8442 g. AgI.
2. 0,3046 g. „ 0,6296 g. „

	Found:		Calculated for $(OCH_3)_2$: for OCH_3 :	
	I	II		
OCH_3	34,08%	27,38%	31,63%	15,81%

It was further proved by the preparation of an acetyl product as well as of a methyl derivative that the body contained a hydroxyl group.

The acetylation was carried out in the usual manner by boiling with acetic anhydride under addition of sodium acetate. The product melted at 106 to 107° , and upon combustion gave the following figures: —

1. 0,1484 g. subst.: 0,3250 g. CO_2 , 0,0846 g. H_2O .
2. 0,1506 g. „ 0,3296 g. „ 0,0899 g. „

	Found:		Calculated for $C_{12}H_{14}O_5$:
	I	II	
C	59,70%	59,69%	60,50%
H	6,33%	6,04%	5,88%

The methyl derivative was obtained by boiling the sodium salt with methyl iodide in alcoholic solution. It melted at 103° and upon analysis gave the following values: —

1.	0,1505 g. subst.:	0,3443 g. CO_2 ,	0,0939 g. H_2O .
2.	0,1620 g. „	0,3708 g. „	0,1005 g. „
Found:		Calculated for $\text{C}_{11}\text{H}_{14}\text{O}_4$:	
	I	II	
C	62,37%	62,34%	62,86%
H	6,77%	6,85%	6,67%

A methoxyl determination gave the following values: —

0,3965 g. subst.:	1,3576 g. AgI .
Found:	Calculated for $(\text{OCH}_3)_3$:
OCH_3 45,37%	44,30%

Treated with bromine in a chloroform solution, the phenol forms a bromide, $\text{C}_{10}\text{H}_{11}\text{O}_4\text{Br}$, m. p. 187° . This combination crystallises from hot alcohol in yellow crystals. The bromine determination gave figures which agree with those theoretically required.

1.	0,1581 g. subst.:	0,1076 g. AgBr
2.	0,1853 g. „	0,1270 g. „
3.	0,1770 g. „	0,1259 g. „

Found:		Calculated for $\text{C}_{10}\text{H}_{11}\text{BrO}_4$:	
	I	II	III
	28,96%	29,16%	30,28%
			29,09%

The preparation of an oxime from the phenol $\text{C}_{10}\text{H}_{12}\text{O}_4$ proved the still remaining fourth oxygen atom of the phenol molecule to belong to a CO-group. For this purpose the phenol was boiled for several hours with hydroxylamine hydrochloride and alcoholic potash. The oxime which separated when acid was added melted, when purified by means of dilute alcohol, at 108 to 110° . It is coloured dark-red by ferric chloride. The results of combustion agree with the formula $\text{C}_{10}\text{H}_{13}\text{O}_4\text{N}$: —

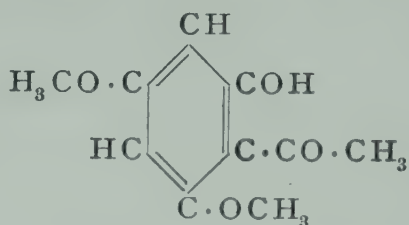
0,1532 g. subst.:	0,3170 g. CO_2 ,	0,0856 g. H_2O .
0,1657 g. „	9,75 cc. N (16° , 742 mm.).	
Found:	Calculated for $\text{C}_{10}\text{H}_{13}\text{O}_4\text{N}$:	

C	56,39%	56,87%
H	6,20%	6,16%
N	6,60%	6,63%

Attempts to obtain a semicarbazone remained fruitless.

From the above results it is evident that the body $\text{C}_{10}\text{H}_{12}\text{O}_4$ contains, in addition to two methoxyl groups, a ketone group, and a

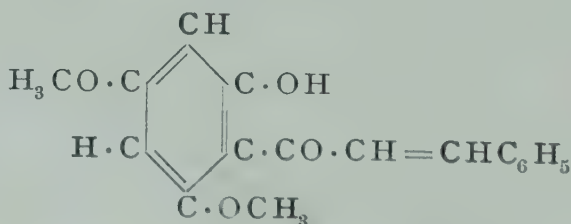
phenol group. Hence it shows, particularly also in its other physical properties, a great similarity to phloracetophenone dimethyl ether, a body first prepared from phloroglucinol trimethyl ether by Friedländer and Schnell¹⁾ and afterwards studied more thoroughly by von Kostanecki and Tambor²⁾. As is apparent from its mode of preparation, this body possesses the following constitution: —



Closer comparison of the phenol which occurs in Ngai camphor oil and its derivatives with the corresponding derivatives of Kostanecki's phloracetophenone dimethyl ether shows that the identity of these two phenols no longer admits of doubt, for the melting points of the phenol, its acetyl product, etc., completely agree with those of the corresponding derivatives of the synthetic phenol. Finally, the question of the identity of both bodies was clinched by the preparation of the 2-hydroxy-4,6-dimethoxychalkone, the product of condensation of phloracetophenone dimethyl ether with benzaldehyde. This combination, prepared according to Kostanecki's directions from the natural phenol, presented itself in yellow crystals, m. p. 91 to 92°, and possessed the same properties as that prepared synthetically. Combustion gave the following figures: —

Found:		Calculated for $\text{C}_{17}\text{H}_{16}\text{O}_4$:
C	71,94%	71,83%
H	5,78%	5,63%

This body has the following formula: —



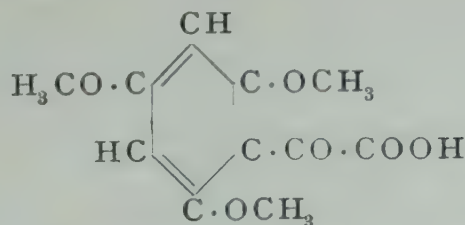
The acetyl product prepared therefrom also possessed a melting point of 130°, which is that already indicated by Kostanecki.

The trimethyl ether obtained from the phloracetophenone dimethyl ether could be oxidised with 3,3 per cent. permanganate solution at

¹⁾ Berl. Berichte **30** (1897), 2152.

²⁾ Ibidem **32** (1899), 2262.

water-bath temperature into an acid, $C_{11}H_{12}O_6$, m. p. $155,5^\circ$, of which the formula is clearly as follows: —



This acid, upon being melted, gave off carbonic acid and carbon monoxide. When submitted to dry distillation it yielded a residue melting at 49 to 50° , insoluble in sodium carbonate solution, which gave a blue colour with fuming nitric acid. Of this acid a quite considerable proportion could be obtained (36 g. from 43 g. ether) and it was easily purified by recrystallisation from hot water. It contained no water of crystallisation.

Combustion: —

1. 0,1682 g. subst.: 0,3390 g. CO_2 , 0,0867 g. H_2O .
2. 0,1471 g. „ 0,2956 g. CO_2 , 0,0721 g. H_2O .
3. 0,1574 g. „ 0,3169 g. CO_2 . —

	Found:			Calculated for $C_{11}H_{12}O_6$:
	I	II	III	
C	54,96%	54,79%	54,91%	55,0%
H	5,73%	5,37%	—	5,0%

The silver salt, recrystallised from water, formed colourless needles, which, however, quickly turned yellow when exposed to light.

0,1993 g. subst.: 0,0618 g. Ag.

	Found:	Calculated for $C_{11}H_{11}O_6\text{Ag}$:
Ag	31,01%	31,12%

As a ketonic acid, this acid when treated with sodium carbonate and hydroxylamine according to Bamberger's directions, yielded an oxime, m. p. $88,5$ to 93° . A nitrogen determination of the body gave the following result: —

0,1444 g. subst.: 7,2 cc. N (20° , 756 mm.).

	Found:	Calculated for $C_{11}H_{13}O_6\text{N}$:
	5,67%	5,49%

The oxime was sparingly soluble in water and ether, but dissolved very readily in benzene.

J. J. Weber, Leipzig.

SEMI-ANNUAL REPORT
OF
SCHIMMEL & Co.
(FRITZSCHE BROTHERS)

MILTITZ

NEAR LEIPZIG

LONDON • NEW YORK.



APRIL 1910.

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List of abbreviations.

d = specific gravity.

$d_{20^{\circ}}$ = specific gravity at 20° , compared with water at 15° .

$d_{\frac{20^{\circ}}{4^{\circ}}}$ = specific gravity at 20° , compared with water at 4° .

$\alpha_{D20^{\circ}}$ = optical rotation at 20° , in a 100 mm. tube.

$[\alpha]_D$ = specific rotation.

$n_{D20^{\circ}}$ = index of refraction at 20° .

Sol. p. = solidifying point.

M. p. = melting point.

B. p. = boiling point.

n = normal.

Acid no. = acid number; ester no. = ester number; sap. no. = saponification number.

g. = gram; cc. = cubic centimeter; mm. = millimeter.

Temperatures are uniformly given in degrees Centigrade.

The strength of alcohol, if not otherwise indicated, is given in per cent. by volume.

The upward commercial and industrial movement of the year 1909, now that the business results can be surveyed, is seen in an even more favourable light than we had dared to expect at the time of writing our last Report, and we are able to state with pleasure that a retrospect upon this additional year of strenuous work and zealous onward endeavour affords a view which is in every respect satisfactory. A year ago we were able to express the conviction that the gradual improvement in the economic conditions of Germany, which was perceptible at the time, would continue to make healthy progress, and our expectations have not been disappointed. The subsequent course of business during the year plainly showed that the stagnation of 1908 had been finally overcome, and that important preliminary conditions for the continuation of a healthy development had been fulfilled. Fortunately the revival has developed slowly and surely, as indeed from the condition of affairs we had expected it to do. Business transactions have moved within the four corners of a normal demand, and have not been disturbed by speculative undertakings. It is to be hoped that the year which has now commenced will continue free from unlooked for incidents, and so far the prospects are exceedingly good, the exports for the first quarter justifying the most favourable expectations. The severe tension which weighed upon Europe at the beginning of 1909 has in the meantime given way to a beneficent restfulness, and, (except for the fact that recently the possibility of warlike complications in Eastern Asia caused us to cast a somewhat anxious eye towards the late theatre of the great struggle between two powerful nations,) there do not appear to be any immediate indications warranting the fear of danger to the peace of the world. As in the preceding year, the leading civilised countries are too much occupied with their internal affairs than that their populations should harbour any desire for adventures outside their own boundaries. Here in Germany, too, the problem of financial reform has caused considerable unrest of late, and its regrettable consequences have thrown a serious and much-felt obstacle into the way of the development of business which had begun to show itself. The economic requirements of a nation

¹⁾ The commercial part of this Report has been compiled during March.

whose agricultural population has fallen within a quarter of a cent (from 1882 to 1907) from 42 % to 28 % of the total, while that part of its people who occupy themselves with commerce and industry has increased in the same period from 45 % to 56 %, certainly deserve better appreciation than was shown in the manner in which the reform in question was carried out. The easy feeling in the money market, which has fortunately prevailed for the last few months is the principal factor in the further healthy development of industry. The fact that the quotations of our leading Public Debt have been weak throughout the time under review is in our opinion an indication of a generally improved industrial tendency, especially because, as is evident from many reports, this ease is not caused by the market being flooded with new loans, but rather by the fact that the investing public is again confidently placing capital in industrial undertakings. Further, when we turn our eyes to the United States — the largest and most desired of all the world's markets — we behold an extraordinarily cheerful picture of steady revival everywhere and experience has sufficiently shown that the condition of business in the U. S. invariably exercises a corresponding influence upon the trade and industry of Europe. From the details given below, it will be seen that the American commercial barometer is firm at "fine weather".

The imports of essential oils into Germany have again shown a not inconsiderable decline during the year 1909; on the other hand the exports have taken an important step in advance. Based upon our own experience, we regard this condition of things as a further proof that consumers in general throughout the year 1909 have adopted the policy of using up the still remaining important stocks of crude oils, and that on the other hand the sale of the essential oils which are manufactured in Germany has increased in a satisfactory manner exceeding, in fact, the totals for the record year 1907.

	1909	1908	1907
Imports	755800 kilos	911300 kilos	1498600 kilos
Exports	508000 „	390800 „	491700 „

The statistics relating to the imports and exports of artificial perfumes show an increase over 1908 in every department, the total amounting to

420100 kilos for 1909
against 280000 „ in 1908

while the imports increased from

11300 kilos in 1908
to 16100 „ „ 1909.

Referring now to the question of commercial treaties, which is one of the very greatest importance for the sale of our manufactures abroad, we may express the hope that in the future new proposals for such treaties will be submitted to the judgment of genuine commercial and technical experts while they are still in the intermediate stage of negotiations, in order that such disappointments may be avoided as commonly attend commercial treaties which are concluded by officials over the heads of those whose interests they affect. The recent treaty between Germany and Portugal was a special case in point.

We are again able to give a favourable report of the work accomplished by our Austrian branch-factory in Bodenbach, although unfortunately the unsatisfactory conditions which prevail in the spirit-industry in Austria and Hungary have experienced no improvement. We have on many previous occasions expressed regret at these conditions, which are of particular importance to us because, as is well known, the spirit-industry is the principal consumer of our manufactures in the Austro-Hungarian monarchy. Nothing definite has yet been heard with regard to the increase in the spirit duty which has been projected for some considerable time; and generally speaking the Austrian Parliament last year, owing to continued obstruction, bitter racial animosity and constitutional crises, has not exhibited itself to great advantage. It is a matter of sincere regret that internal disagreements have prevented our neighbouring and allied monarchy enjoying the fruits of the notable victory which it had gained in foreign politics.

In the course of the past year there has been a noticeable commercial improvement in the United Kingdom, and our London branch office has been extremely busy. The Board of Trade statistics of the first months of the present year also show an increasing volume of trade, and in general — notwithstanding the continuance of the unsatisfactory conditions in the soap industry to which we have already previously referred — the prospects might be called highly satisfactory were it not for the confusion reigning in the home politics of the United Kingdom. It will need the exertion of the nation's utmost powers to overcome the crisis which will ensue upon the expected fresh dissolution of Parliament — a crisis in which the economic life of the country is bound to suffer. The preliminary commercial arrangement between Great Britain and Germany, which expired on 31st December 1909, has been renewed for 2 years, and until the conclusion of this period at any rate, there is thus no fear of fiscal complications. It is a matter of congratulation that the Chamber of Commerce in London has decided to take steps for the establishment of a special German section, the particular object of which will be the removal of misunderstandings and difficulties in commercial transactions with Germany and an improvement in the general relations between the two countries.

In the British Colonies business has run a regular course, and in British India especially the volume of transactions indicates healthy improvement. It seems likely that in the near future the commercial condition of that country will undergo a further favourable development, for the cotton and oil-seed crops have been good. According to experience, under such conditions new firms grow up in India like mushrooms, and the greatest care is necessary in establishing commercial relations. One of the sons of our senior partner has made a journey to India and Australia, which has again afforded us an opportunity of obtaining a personal insight into the conditions prevailing in those markets. In doing so we have gathered a number of interesting facts, which should be of particular interest to our customers in the perfumery industry; and we shall probably return to this subject on another occasion.

It is of course a matter of particular interest that after a duration of twelve years, the commercial war between Germany and Canada, which has afforded so much occasion for regret, was concluded on 15th February 1910 by a preliminary agreement, an *interim* treaty having been concluded which will run from 1st March 1910 to 31st December 1911, unless previous to its expiration a final commercial treaty between Germany and Canada should have been signed. It is common knowledge that under this agreement the surtax of $33\frac{1}{3}\%$ which has been levied upon all German produce since 1903 is removed. The extreme severity of the effects of the tariff war are shown by the fact that during its continuance German exports to Canada fell from 38.7 million marks in 1902 to 20.3 million marks in 1908, that is to say by nearly 50%. Fortunately the important Canadian market will now again be reopened to our industry.

The sale of our manufactures in France was exceptionally brisk towards the end of the year. It commenced with what can only be described as a run on vanillin, caused by the fact that it was at first supposed that the Government decree affecting this article (see our Report for October 1909, page 142) would become operative as early as 1st January 1910. In addition to this there was the threatening imposition of the new French Customs tariff, one of the consequences of which was an extremely lively demand for our manufactures, especially those of the more expensive kinds. It is much to be regretted that the projected changes in Customs duty have been especially heavy so far as our articles are concerned, and we are justified in looking with great anxiety upon the future of the French market, which, especially for our industry, is an exceptionally important one. We still indulge in the hope that some attention will be paid to the representations of German industry, which is being heavily hit in almost all its branches, for there is no doubt whatever that unless this is done, corresponding reprisals will be taken by Germany and a serious tariff crisis will be created.

between the two countries. Such an eventuality would destroy at one blow the revival of mutual sympathy to which it has been so often our pleasure to call attention in these Reports, and a state of tension would thus be created between the two nations, the economic consequences of which for both sides it is impossible to foresee.

The commercial crisis under which Spain has suffered for several years still continues, and its end is not yet in view, all hopes of improvement in the economic conditions being so far unfortunately entirely illusory. It is true that the spring of 1909 began with prospects of a good harvest, but in the course of the summer the greater part of the crops were destroyed by long-continued drought. The misfortunes of the country were further increased by the outbreak of a totally unexpected war with Morocco, which withdrew an army of 50000 men from the country for several months, and lightened the Exchequer by many millions. But the uncertain state of Spanish home politics which weighs so heavily upon Spain has long been, and still remains, by far the greatest enemy of the country. It completely paralyses all trade and commerce, nips in the bud all serious endeavour towards industrial improvement, and compels capitalists who have any desire to embark upon undertakings in Spain to exercise the greatest imaginable caution. Throughout Spain, in small as well as in large matters, private interests are considered far more than those of the public, and ministries, generally constituted without any well-considered programme, follow each other in rapid succession, often within the space of a few months, and disappear before they have even had the time to form a clear idea of the existing conditions. The perfumery industry of the country, which is of much importance for us, shows a noticeable growth and improvement from year to year, less so the industry of soap manufacturing, particularly as regards the better qualities; while the industry of liqueur-making is steadily dwindling towards extinction under the pressure of the existing spirit law.

There is no need to refer in detail to the other European markets, in all of which we have experienced increased sales. In Holland, Switzerland and Italy the conditions have been normal throughout the period under review, only the Balkan States continue to present the familiar picture of political uncertainty. Owing to military preparations on both sides, the relations between Turkey and Bulgaria have been strained, but in the meantime an understanding has been established between these two Powers; on the other hand, the possibility of a fresh war between Turkey and Greece has recently been a matter of frequent comment. There is no doubt, however, that timely intervention by the Great Powers, who are anxious for the maintenance of peace, will succeed on this as on previous occasions in removing the threatening danger.

Stimulated by a favourable harvest, the sale of our products Russia has continued to be extremely satisfactory within the last months, but business has suffered decidedly owing to severe competition which moreover in many quarters has been conducted by means which were not always free from objection. The largeness of the requirements of the important Russian drug firms has repeatedly induced certain houses in our branch to approach these customers with goods of a quality which reflects little credit upon our industry, and we cannot allow this opportunity to pass without again urgently warning our Russian friends against such "exceptionally advantageous" offers. Up to the present the projected revision of the Russian Customs tariff has not entered upon a new stage. We refer below to the fears which have lately been entertained of the possibility of a fresh Russo-Japanese conflict.

As already mentioned in the opening sentences of this introduction the hopes expressed in our last Report with regard to the commercial position in the United States have been confirmed in every respect and our New York branch is able too look back with ample satisfaction upon the results of its endeavours to promote the sale of our manufactures in this market, for which, after a commercial relationship extending over nearly 40 years, we entertain feelings of something more than mere business connection. The fact that in spite of the well-known severity of competition the turnover of our branch-house exceeded even the figures of the record year 1907, probably affords the best proof that the popularity of our products is still growing. After the coming into force of the new American Customs tariff a few slight surprises occurred, which had escaped attention upon the publication of the new law. Although these surprises were not of an important nature, they yet had to some extent a disturbing effect upon business. We will only refer here to the rather remarkable classification of Sweet Orange Oil, which has been made dutiable at the rate of \$ 1 per lb. as "Fruit Oil", instead of (as was generally expected) at the rate of 25% *ad valorem* which applies to essential oils. Ostensibly this high duty has been enacted in the interest of the Californian orange growers but the American Government ought to have made itself acquainted with the fact that it will probably never be possible to manufacture orange oil in California on a competitive scale, because the process of hand-pressing cannot be avoided, and manual labour is so dear in the United States that even a protective duty of \$ 1 per lb. will be of no effect so far as this industry is concerned. It goes without saying that the consumers have protested against the duty, and that since the tariff has come into force all imports have been left in bond. Fortunately considerable stocks of old oil were available, and by slightly limiting the consumption it was possible to make shift with these

In all probability, before this Report appears the American Government will have given a final decision as to what rate of duty is to be applied to the article. It is further evident that the clause in the new tariff making the receptacles in which goods are packed liable to duty is not hailed with particular joy by firms who are concerned in importation. So far as can be judged from the result of the first three months of the year, the general business outlook is extremely satisfactory, and the German-American Commercial *proviso* which came into operation on 7th February will powerfully assist in further stimulating business. Under this agreement Germany will for the present enjoy the most-favoured-nation clause, and the tariff war which threatened at one time — and the consequences of which upon the whole German export trade to the U. S. would have been incalculable — is avoided.

Imports and Exports of Essential Oils into and from the
United States in the second half-years 1909 and 1908.

Imports			Exports		
	1909	1908		1909	1908
July	{ Duty-free \$ 67 656 Dutiable „ 33 067	{ \$ 138 288 „ 29 745	July	{ Peppermint oil \$ 16833 Other indigenous oils „ 18 390 Foreign oils, duty-free „ 3 844 „ „ dutiable „ 1 174	{ \$ 16 201 „ 16 599 „ 424 „ 1765
Aug.	{ Duty-free „ 147 444 Dutiable „ 42 093	{ „ 123 285 „ 34 592	Aug.	{ Peppermint oil „ 7411 Other indigenous oils „ 23 512 Foreign oils, duty-free „ 1 588 „ „ dutiable „ 1 098	{ „ 16 384 „ 12 023 „ 1 616 „ 350
Sep.	{ Duty-free „ 77 650 Dutiable „ 42 602	{ „ 208 873 „ 44 534	Sep.	{ Peppermint oil „ 16 360 Other indigenous oils „ 22 374 Foreign oils, duty-free „ 1 162 „ „ dutiable „ 2 113	{ „ 42 696 „ 25 054 „ 6 579 „ 1 623
Oct.	{ Duty-free „ 58 743 Dutiable „ 46 049	{ „ 130 918 „ 36 777	Oct.	{ Peppermint oil „ 32 601 Other indigenous oils „ 34 309 Foreign oils, duty-free „ 4 454 „ „ dutiable „ 1 415	{ „ 36 822 „ 24 578 „ 667
Nov.	{ Duty-free „ 101 428 Dutiable „ 57 038	{ „ 157 424 „ 31 741	Nov.	{ Peppermint oil „ 43 063 Other indigenous oils „ 38 054 Foreign oils, duty-free „ 2 198 „ „ dutiable „ 1 504	{ „ 33 001 „ 26 737 „ 1 301 „ 652
Dec.	{ Duty-free „ 94 368 Dutiable „ 67 515	{ „ 163 113 „ 43 960	Dec.	{ Peppermint oil „ 21 234 Other indigenous oils „ 24 357 Foreign oils, duty-free „ 1 225 „ „ dutiable „ 1 668	{ „ 44 422 „ 28 594 „ 1 595 „ 1 056

Total value of Imports in 2nd half-year 1909	\$ 835 653
„ „ „ „ 2nd „ „ 1908	„ 1 143 250
„ „ „ „ whole year 1909	„ 2 564 915
„ „ „ „ „ „ 1908	„ 2 933 222
„ „ „ Exports „ 2nd half-year 1909	„ 321 941
„ „ „ „ „ „ 1908	„ 340 739
„ „ „ „ whole year 1909	„ 600 399
„ „ „ „ „ „ 1908	„ 610 883

It is well known that among the South American Republics Argentina — which celebrates its centenary this year — is of

special importance, as regards the consumption of our products. In the course of the past year the demand from the Argentine Republic has continued to be brisk, the economic condition of the country having again been satisfactory, and although the quantity of cereals exported was below that of 1908, the falling-off was compensated by the high prices of all natural products, and by an increased export of cattle. Unfortunately the revision of our commercial relations with Argentina — which would be hailed with satisfaction by all those who are interested in the export trade to this important country — still remains in abeyance, although there is no doubt whatever that the existing commercial treaty is by no means sufficient for either of the parties concerned. In the course of the last ten years the excess of Argentine exports to Germany over the imports from this country has almost trebled, which is a sufficient proof that the Argentine Republic must be greatly interested in the continuance of its good commercial relations with us. It has recently been rumoured that Argentina has held out to the United States the expectations of certain commercial concessions, and in view of the business relationship depicted above, it seems probable that such concessions should also be obtainable by Germany. According to the *Buenos Aires Handelszeitung* of 5th February 1910, the harvest of 1909—10 has not come up to the expectations which had been entertained from the favourable state of the crops in November, for after the end of that month damage was caused, first by drought and afterwards by frost. Unfortunately this news as to the quantitatively unfavourable result of the harvest is not likely to remain without its influence upon business. In Uruguay the position last year has been equally favourable. The principal source of wealth of this country is cattle, and in the first half of 1909 this also suffered considerably from the drought which was experienced here as in Argentina. Afterwards, however, favourable weather set in, although this was accompanied by a passing plague of locusts. According to information supplied by the *Deutsche Ueberseeische Bank*, the imports and exports of Uruguay have been as follows: —

	Exports	Imports
1909 about	\$ 45700000	\$ 37100000
1908 " "	40300000	34600000.

Business with Chili shows a further increase, but transactions in this country do not always pass off without loss, for the consequences of the earthquake of 1906 have not yet been entirely surmounted, and recently a serious fire in Valdivia has caused considerable damage in this town, especially in German business circles. Unfortunately so far no measures whatever have been taken to place the rate of exchange upon a firm footing, and the prevailing condition of uncertainty and

of incalculable fluctuations in the exchange is likely to be prolonged for an indefinite time.

From an article in the *Deutsche Export-Revue*, which gives a characteristic account of the unexampled conditions still prevailing in the Chilian ports, conditions to which we have repeatedly referred on previous occasions, we quote the following: —

“Both shippers and merchants complain bitterly of the shameless manner in which cargoes are treated in the various ports of the West Coast of South America. Thefts are so frequent and so extensive that the Pacific Steam Navigation Company reports having already paid out £ 20000 as a result of these robberies, in spite of the fact that on several occasions it has made representations on the subject to the Peruvian and Chilian Governments through the Foreign Office. The thefts commence on board ship, are continued in the lighters and only end on shore. Recently, in a Chilian port, it was found that a parcel of corrugated iron had disappeared; on the following morning the goods were discovered, being then already in use as a roof for a building which had just been erected! In another port the robbers seized a boat in broad daylight and pitched its contents into the sea, where they were spoilt by the salt water. The majority of carmen and day-labourers are actively concerned in these robberies. In many cases the stolen goods are sent up-country, where they are exchanged for liquor. At Callao the goods are unpacked on the quay and stolen there. The watchmen are so badly paid that they have no scruples in increasing their income by making common cause with the thieves and at night, together with them, pilfering the packages entrusted to their care. At Antofagasta shops have been opened expressly for the sale of stolen goods. The fact that a few weeks ago, at Talcahuano, a whole lighterful of merchandise was spirited away, in order to enable the thieves to rob at their ease several cases of fancy-goods which had been packed with particular precaution, goes to show that the safeguards for which foreign traders are fairly entitled to ask, are not even remotely observed. No improvement in this state of things can be looked for until the protection of the shore is entrusted to the military, with the right to shoot out of hand any marauders caught in the act. Armed motor-boats would no doubt be able to suppress promptly the piracy which is now rampant.”

Agriculture is able to look back upon a favourable year, as a result whereof business has been brisker, especially in Central and Southern Chili, but the nitrate districts of the North, in sympathy with the market-position of their principal products, have not been so flourishing. The linking-up of railway communication with Argentina which is about to be effected, will be of far-reaching commercial importance, and will bring the Chilian market much closer to our doors.

In Peru the recovery of business is still being delayed. This country continues to suffer from the consequences of last year's disturbances and of the frontier-dispute with Bolivia and has not yet quite succeeded in regaining the confidence of those firms in Europe which are interested in its commercial affairs.

In Brazil our trade has experienced a further marked improvement and so far nothing is being heard of any change in the fiscal policy of this important consuming market. Protected by high duties, Brazilian

home-industries are making fair progress, and in many German industries complaints are rife of a falling-off in the exports to Brazil. So far as regards our products, which are not finished manufactures but mainly the semi-manufactured goods needed for use in various industries, a healthy increase can be reported, and we are therefore unable to join in the complaints referred to. It so happens that the United States, who enjoy preferential treatment under the Brazilian tariff, are not able to supply much in the way of essential oils and perfumes, hence competition from that quarter is but little felt in our branch.

Mexico would certainly have made further headway last year towards the reattainment of its former favourable economic situation if the country had not suffered serious injury from the alarming earthquakes in the State of Guerrero, and from widespread floods in other districts, but the preliminary conditions exist for a quiet and safe development and we may therefore look hopefully towards the future of this valued market.

Our business-relations with Japan have undergone a very brisk development in the course of the last few months, and in this market, which possesses such a high purchasing-power, the turnover for the entire year also shows a marked advance. It is true, however, that the favourable expectations of the second half of the year 1909 have not been realised in their entirety, and that enterprise has been retarded by a pronounced attitude of reserve, which has only lately given way to a more confident feeling. A wholesome revival is generally looked for in the course of the present year, always presuming that the expectations of good rice- and silk-harvests are not disappointed. The rumours of warlike complications which have recently been circulated in certain European and American papers with political objects appear to have found little or no echo in Japan itself. The harmful consequences and severe consequences of the war are still so fresh in the recollection of the Japanese people that no effort will be spared to prevent as far as possible any return of such a national calamity. There are probably among the military party some swash-bucklers who think differently, but they will not have enough influence to convert their light-hearted desires into deeds unless, indeed, a foreign power should become the aggressor. The latest reports appear to point to the conclusion, in the immediate future, of a definite understanding between Russia, China, and Japan on the Manchurian question, and, as regards Korea, it is generally expected that the present Japanese protectorate will shortly be followed by definite annexation, a step which, according to competent observers, can only be to the advantage of the Koreans. The Japanese Government has already last year redeemed its promises of retrenchment in the ex-

enditure on the army and navy and appears to be trying to lighten the burden of national taxation and to remove, or at any rate reduce, unpopular imposts.

We have before us a report, dated from the beginning of February of this year, on the subject of the Japanese soap-industry in 1909. Its purport is that, generally speaking, business in this branch has been very satisfactory. Raw materials were cheaper than in 1908, and owing to the brisk demand there was no necessity for reducing the selling-prices of the finished goods. It is said that, during the second half of the year, the exports to China were lagging somewhat, but that recently several Japanese soap-makers, especially among those who manufacture transparent soaps, have established branch-factories in China, in order to avoid the high Japanese duties on spirits and sugar, which increase the cost of manufacturing in Japan.

The question of the impending revision of the customs tariff, which has a place on the programme of the Japanese Government for the present year, is naturally of high importance for the further development of German trade with Japan. As is well known, Japan intends to abrogate its commercial treaties in the summer of next year, before they actually expire, and the new tariff is accordingly to come into force in July or August 1911. The draft-scheme contains several proposed alterations in goods such as we manufacture, but we consider it premature to express an opinion thereon, as we are informed that the proposals are of a preliminary character and as the new law is as yet under consideration. Different views prevail with regard to the tendency of the tariff; but we think we may rely upon the statesmanship of the legislators to deal considerately with articles of our branch, seeing that they are merely used for manufacturing purposes and that it is of great importance for the industries of Japan to be able to obtain them on advantageous terms.

Commercial notes and scientific information on Essential Oils.

Oil from the leaves of *Aegle marmelos*. According to a communication by Ritsema¹⁾, the leaves of the *Modjo* tree (*Aegle marmelos* Corr., N. O. Rutaceae), are regarded by the natives of the Island of Madura as a remedy in foot-and-mouth disease. The leaves yielded about 0,6% of a faintly yellow-coloured oil ($d_{25^{\circ}}$ 0,856; $\alpha_{D26^{\circ}}$ + 10,71°; sap. no. 10,6),

¹⁾ Jaarboek van het Departement van Landbouw in Nederlandsch Indië 1908, p. 52.

which was divided into the following fractions: I. b. p. up to 105 g.; II. b. p. 100 to 130°, 5,1 g.; III. b. p. 130 to 160°, 1 g.; IV. sidue 1,5 g.

Fraction II contained d-limonene, which was identified more accurately by its b. p. (175°), and its tetrabromide (m. p. 104 to 105°). No aldehydes could be detected in the oil. A peculiar feature of this oil is that when left exposed to the air about a quarter an hour it loses about 8% of its original weight and turns very cloudy. When allowed to stand a considerable time, the oil again becomes clear, but assumes a viscous, resinous condition. A similar viscous product was obtained from the dried leaves by distillation.

Almond Oil, pressed, from apricot kernels. The market for apricot kernels has not undergone any noticeable changes since our last Report. The prices were maintained at about 70 marks per 100 kilos, and although transactions in kernels in the months of October and November were more brisk this had no effect worth mentioning upon the market. As a result, the quotations both for pressed and for essential oil of bitter almonds have remained unchanged. Quite recently apricot kernels of Japanese origin have now and then been offered at about 65 marks per 100 kilos, and although the quality of this merchandise cannot be compared with that of the finest kernels from Damascus, we would nevertheless advise the growers in Syria to give attention to this new competition in good time, as otherwise, assisted by the higher prices, it may develop so powerfully that before long it will become a factor of some importance in determining the prices. There is probably no room for doubt that Japan is able to produce considerable quantities.

Almond Oil, pressed, from almonds, Ph. G. IV. The prices of sweet almonds have fortunately not been able to maintain themselves at the figures which they reached last autumn, and when it became evident that the rumours of a shortage of the crop in the principal producing districts were greatly exaggerated, the market in the course of November gradually receded to about 190 marks per 100 kilos for best Bari quality, Sicilian almonds being correspondingly higher in price. Since then the values have remained about the same and the quotations for our sweet almond oil, pressed by ourselves, have been reduced in proportion. The season is not yet sufficiently advanced to enable us at the present time to give an opinion of the prospects for the current year. We feel a not unnatural pride in the fact that our prolonged efforts, extending over many years, to re-establish reputable methods of trading in the almond oil business have resulted in a steady increase in our turnover, which makes it occasionally very difficult for the capacity of our plant to keep pace with

ar sales. It is necessary to continue to lay stress upon the fact that it is always desirable to buy this delicate article direct from the manufacturers; for by doing so purchasers will avoid the unpleasant consequences which very often result from the storage of the oil in the middleman's warehouse.

In our last Report¹⁾ we called attention to the contradictory results of the observations of Auld and of Feist, inasmuch as Auld had found that the synthesis of d-benzaldehyde cyanohydrin can be accomplished more rapidly than its generation from amygdalin, while Feist arrived at the opposite conclusion. The last-named investigator returns to the matter in his latest publication²⁾. He has repeated his earlier experiments and has now discovered, in agreement with Auld, that d-benzaldehyde-cyanohydrin can actually be prepared synthetically more quickly than by splitting-up amygdalin, but he states that the course of the reaction depends upon the quality of the emulsin employed. When using Schuchardt's emulsin he obtained precisely the same results as before, while with Kahlbaum's emulsin the result was the reverse. It would appear that in Schuchardt's emulsin the enzyme predominates which influences the process of decomposition, and in that of Kahlbaum the synthesis-influencing enzyme. Thus the question would appear to be re-opened whether, in the splitting-up of amygdalin, d-benzaldehyde cyanohydrin is formed primarily or secondarily.³⁾ In order to solve this problem, Feist instituted experiments with a d-emulsin prepared according to Rosenthaler's⁴⁾ method, treating with it not only amygdalin, but also such quantities of hydrocyanic acid and benzaldehyde as are required for the preparation of benzaldehyde-cyanohydrin. The action of emulsin upon amygdalin caused a slight rotation to the right, but in the benzaldehyde-hydrocyanic mixture no optical rotation could be observed. But this result, although pointing to the primary generation of benzaldehyde-cyanohydrin from amygdalin, was scarcely sufficiently convincing, owing to the slowness of the rotation ($\alpha_D + 0,15^\circ$).

Feist has also in part repeated Walker and Kriebel's⁵⁾ experiments in splitting-up amygdalin with various acids. He likewise found that when amygdalin is treated with sulphuric acid, the sugar is first split off with generation of d-benzaldehyde-cyanohydrin. It is therefore necessary, when conducting experiments in decomposition by means of emulsin, to consider the presence of the d-benzaldehyde cyanohydrin complex in the molecule of amygdalin.

¹⁾ Report October 1909, 20.

²⁾ Arch. der Pharm. 247 (1909), 542.

³⁾ Comp. Report November 1908, 15; April 1909, 17; October 1909, 20.

⁴⁾ Biochem. Zeitschr. 1909, 71.

⁵⁾ Journ. chem. Soc. 95 (1909), 1369; Report October 1909, 23.

Some years ago, Walker¹⁾ discovered that amygdalin is converted by the action upon it of a small quantity of alkali, into a more readily soluble compound, to which he gave the name of rac. amygdalin. Under hydrolysis, this body yielded rac. mandelic acid. Recently Walker has continued his investigation in collaboration with V. K. Krieble²⁾. They succeeded in isolating from the racemic compound a crystalline body from which, by hydrolysis, they obtained l-mandelic acid, while hydrolysis of the mother-liquor of the same body resulted in the isolation of d-mandelic acid. Rac. amygdalin, therefore, is not a uniform body, but a mixture of d- and l-amygdalin. Further examination, however, showed that the racemisation of amygdalin with alkali is a highly complicated process, for simultaneously with it, β -glucoside is partly converted into α -glucoside. This fact renders examination very difficult and makes it improbable that rac. amygdalin consists of a simple mixture of d- and l-amygdalin.

Angelica Oils. In spite of the apparently favourable conditions of the angelica fields in Saxony and Thuringia last autumn, the crop has again caused great disappointment. Although as regards the quantity of material harvested the expectations were more or less realised, the yield of oil was so poor that the quantity which could be distilled was quite insufficient for the requirements. Our angelica fields, at Miltitz also, in spite of their very satisfactory appearance, produced only very little oil and we were therefore compelled later on to buy large quantities of *root*. On all hands the newly distilled oil was being impatiently awaited, hence a considerable demand arose during the distilling season, which resulted in a material advance in prices. Since that time the quotations have risen up to 200 marks per kilo for genuine quality, and as the quantities of oil for disposal are certainly not likely to hold out until the new crop, a further rise in the market can be confidently expected.

The prices asked for angelica *seed* were so exaggerated that up to the present it has been impossible to resume the distillation of this oil, which must therefore continue to remain a blank in our lists.

Anise Oil, Russian. As already stated in our last October Report, the tendency of the market at the first anise-fair was very firm, notwithstanding the favourable results of the harvest. The reason of this was that owing to the poor crop of sunflower-seed the buyers of the last-named article had ample capital at their disposal for speculating in anise. At the second anise-fair at Alexejewka only 75 waggon-loads arrived instead of the 100 which had been expected, and these

¹⁾ Journ. chem. Soc. 83 (1903), 472.

²⁾ Journ. chem. Soc. 95 (1909), 1473.

were bought up at whatever price was asked, so to speak. The supplies came in so leisurely that they were mostly secured at the village entrance by certain speculators, a state of things which had never been known before and which, of course, contributed in a extraordinary degree to give a firm tendency to the article; thus the bulk of the harvest, as already stated, was taken out of the market immediately, on the spot, and this manipulation was favoured by the fine dry condition of the seed, which made it particularly suitable for storing. This year, therefore, the speculators have had decidedly the best of it, and by carefully keeping back supplies and suiting their offers to the demand they have succeeded in driving-up the quotations to a point which makes it impossible for us in Germany to lay in supplies of their aniseed for distilling. It is fortunate that for many years past the oil from Russian anise has been more or less relegated to a second place owing to the competition of pure *anethol*, for which reason high anise prices have long ago ceased to be a serious matter for our industry. It is well known, of course, that other raw materials are available for the preparation of anethol, and therefore only those manufacturers of anethol who, owing to their location, are restricted to its manufacture from Russian seed are seriously inconvenienced by existing conditions.

Artemisia Oil. An oil which has been prepared by Th. Whittelsey¹⁾ from the green branches and leaves of a kind of *Artemisia* (perhaps *A. cana* Pursh.) is of interest on account of the proportion of l-camphor contained in it. The plant, which has its habitat in the Western parts of North America, has a powerfully aromatic odour, and its oil (which Whittelsey obtained in a yield of 1,2%), has the following constants: — d_{15° 0,9405, n_D — 19,09°, n_{D20° 1,4702, acid no. 4,1 to 4,2, sap. no. 22,7 to 23,9, sap. no. after acetylation 110,3 to 111,8. The oil was divided up into three fractions by distillation: I. b. p. 185 to 191°, II. b. p. 191 to 197°, III. b. p. 197 to 203°. The third fraction consisted chiefly of l-camphor (m. p. 174 to 175°; m. p. of the oxime 119 to 120°). This camphor may be separated out even from the original oil by placing it in a freezing mixture; it is present in the oil to the extent of not less than 44,5%, as was shown by determining it in the form of the semicarbazone (m. p. 235 to 236°).

The above is one of the rare cases in which an essential oil has been found to contain l-camphor. Up to the present this compound had been detected only in oils of feverfew, tansy²⁾, *Artemisia Herba-*

¹⁾ Wallach Jubilee publication (Göttingen 1909, Vandenhoeck & Ruprecht) p. 668.

²⁾ Gildemeister & Hoffmann, *The Volatile Oils*, pp. 678—679.

*alba*¹⁾, *Blumea balsamifera*²⁾ and the oil of a species of *Salvia*, possibly *S. grandiflora*³⁾.

Oil of *Barosma pulchellum*. In one of our last Reports⁴⁾ we stated that the oil of *Barosma pulchellum* contains an oily acid m. p. 125 to 131° (5 to 6 mm.), which is probably identical with citronellic acid. The not very exact m. p. of the amide of this acid lies at 87 to 88°. We have now compared it with the amide of citronellic acid, as obtained by Tiemann's method⁵⁾ from the nitrile of citronellic acid by imperfect saponification with alcohol and potash. According to our observations, the citronellic acid amide from citronellal, purified by light petroleum or dilute alcohol, only melts at 84 to 85°, while the amide of the acid of oil of *Barosma pulchellum* melts at 87 to 88°. A mixture of the two derivatives melts as low as 80 to 82°, but in appearance the two amides cannot be distinguished from each other. It would therefore appear that the amide of unsharp m. p. 87 to 88° consists of a mixture of the amide of citronellic acid with traces of an amide of another, (possibly capric acid). At any rate, we were able to ascertain that the citronellic acid from citronellal also boils at 257°, and its chloride (like that of the acid of the above oil), at 122 to 123° (5 to 6 mm.). Hence we regard the two as being identical.

Oil of Sweet Basil. The arrivals are trifling, and consist largely of Algerian and Spanish oils, as the production in Réunion appears to have entirely ceased. Since last year we have been experimenting in the cultivation of sweet basil at Miltitz, and in the course of the coming summer we will be able to distil at least a part of our own requirements. It goes without saying that we shall do our utmost to make the oil of our own distillation equal in quality to the best.

Bay Oil. The position of this article is more or less unchanged, although it has been decidedly noticeable that almost everywhere the production has been diminished, as a result of which a more healthy proportion between demand and supply has prevailed. The prices continue to be very cheap and it is most regrettable that Bay-rum, which was formerly such a popular article, appears to be gradually going out of use entirely.

Birch tar Oil. In a brief market report⁷⁾ on the products of the dry distillation of wood in Russia at the commencement of the last winter-

¹⁾ Grimal, Bull. Soc. chim. III. **31** (1904), 694; Report October 1904, 13.

²⁾ Jonas, Report April 1909, 148 and the present Report, p. 148.

³⁾ Wallach, Nachr. K. Ges. Wiss. Göttingen 1905, 1.

⁴⁾ Report April 1909, 96.

⁵⁾ Berl. Berichte **31** (1898), 2902.

⁶⁾ Tiemann gives the m. p. of the acid as 81,5 to 82,5°.

⁷⁾ Zeitschr. f. angew. Chem. **22** (1909), 2303.

season reference is made to the serious sophistication which takes place in birch tar oil. The report mentions, as an example, that it is the practice to make mixtures in various proportions of common crude tar and of the light tar oils of pitch-boiling, and to impart to the mixtures the greenish fluorescence of birch tar oil by adding sulphuric acid, while genuine birch tar oil is only added to give the required odour. Birch tar oil, however, continues to be in great demand, and as in certain conditions it is extremely difficult to test its purity, dealings in the article are more than ever a matter of confidence in the integrity of the seller.

Cajeput Oil. According to statistics from Macassar, the shipments in the months from January to November 1909 have only been —

	1309 baskets				
against	2920	„	in the year	1908	
	3487	„	„	„	1907
	3419	„	„	„	1906

during the corresponding periods.

It is satisfactory to learn from these figures that efforts have been made to reconcile the supplies with the halting character of the demand. This has already had the effect of considerably reducing the stocks in Europe and the movement of the article therefore has lately again become firm, but oil of cajeput continues to suffer under the competition of the numerous cheap eucalyptus oils, and especially of pure eucalyptol, which has lately been offered at such exceptionally advantageous prices. This competition will make it impossible for the price of cajeput oil again to reach its former high level.

Camphor Oil. The firm tendency which we reported last October has gradually brought about a position previously unknown in this article. The supplies in Europe and the United States have greatly decreased, owing to the strong demand which has existed for all products of camphor oil, and from Japan offers of crude oil have practically been unobtainable. This reticence of the Japanese is said to be based upon the circumstance that it is the intention of the Japanese Government to work up all the crude oil produced in Formosa — which up the present has always been sent to Japan — in the island itself. It is reported that the necessary plant for this purpose will be ready to start work on April 1st, but at the time of going to press further details were still wanting. There is no doubt that if the projected scheme is really carried out it will be of the utmost importance for the whole of the camphor oil business, for it stands to reason that it will be the endeavour of the Japanese Government to make as much profit as possible from the future sale of camphor oil, and, at the beginning

at any rate, the firmness of the tulpentine oil market will assist in this object.

In the meantime the following figures relating to the output and the export have been published: —

Japan. The exports last year up to September amounted to 2519055 kin camphor, of a value of 2136259 yen. This quantity is in excess of that of last year, but owing to the lower prices the total value is less. A continuance of these prices is regarded in many quarters as likely to be ruinous, especially if, as is expected, the manufacture of the artificial product should be improved¹⁾.

In the months from April to November 1909 the production in the island of Formosa amounted to 1988355 kin camphor and 2287703 kin camphor oil. The planting of young camphor trees in the island is making steady progress; in 1906 346000 trees were planted, in 1907 1300000, and in 1908 4830000. Last year 5060184 young trees are reported to have been put in the ground²⁾. According to a report by the German Consulate at Nagasaki³⁾, the value of the camphor exported from Formosa to foreign countries in 1908 was 1710400 yen against 2619100 yen in 1907. The quantity sent to Germany directly represented a value of 44579 yen; in 1907 no direct trade with Germany had yet been opened up. In our last Report we gave particulars from the same source concerning the total exports of Formosan camphor⁴⁾. See also p. 26 of the present Report.

Shortly before closing this Report we found in the *Nachrichten für Handel und Industrie*, published by the German Home Office⁵⁾, the following two interesting articles on Japanese camphor, which we here quote in full.

“For many years the managers of the Japanese Monopoly believed that they would be able to rule the camphor market and to fix the prices of the article. They therefore gradually increased their average selling prices per kilo camphor in Japan from 2.61 m. in the year 1903 up to 4.00 m. in the years 1906 and 1907. At the same time they encouraged the production of camphor to the utmost, partly by increasing the prices at which they bought from the producers, partly by laying down new plantations where the camphor forests were becoming exhausted. Owing to the high prices, however, the Japanese product was being undersold by the artificial German camphor and by Chinese camphor, which latter is only able to compete on a large scale when the market is high. As a result the managers of the Japanese Monopoly have found few buyers for their article since the year 1907. When they became convinced that their plan had failed they decided to lower their prices repeatedly and considerably, in order to get rid of their ever accumulating stock. As a result of this, Japanese camphor is now being sold in

¹⁾ Oriental Druggist, Yokohama 3 (1909), No. 20, p. 2.

²⁾ Ibidem No. 21, p. 2.

³⁾ Nachr. f. Handel u. Industrie 1909, No. 136, p. 1.

⁴⁾ Report October 1909, 30.

⁵⁾ Nachrichten f. Handel u. Industrie 1910, No. 28 and No. 29, p. 5.

London and New York at 135/- to 140/- per cwt., which (allowing 29.40 m. per 60 kilos for freight and sale expenses) is equal to 2.07 m. per 1 kilo in Japan.

It is true that this radical measure has effected a considerable clearance of stock, but on the other hand it has been attended by serious drawbacks, as will be seen from what follows.

Camphor is produced in Formosa and in Japan Proper (Old-Japan), the production of these two sources of supply being as follows: —

Financial year	Formosa	Japan
1906	2847 251 kilos	687 388 kilos
1907	3 603 027 „	733 537 „
1908	—	951 454 „

As far as can be ascertained, the average cost of production to the Monopoly during the last three years has been 3.— m. per kilo in Japan, and in Formosa, after the raising of the buying price in 1906, 1.75 m. per kilo.

It follows that at the costs of production and sale mentioned above the Monopoly in Old-Japan works at a loss. This important fact has been admitted and is avowedly the reason for the limitation and cheapening of the production which commenced in March 1909.

As is natural, the revenue of the Camphor Monopoly in Formosa, which in the financial year 1907 still exceeded £ 200000, has also decreased considerably, and the profit on camphor, the cost of production of which varies according to the districts, has likewise fallen off greatly. If we take into account the costly expeditions against the savage tribes in the island, which have been chiefly undertaken for the purpose of acquiring new camphor forests, it is clear that in Formosa also the Monopoly cannot make both ends meet under the present conditions. It is therefore to be assumed that the Japanese Government intends to restrict the output in Formosa also and, after selling off the present important stocks, to consider an increase in its selling prices. It would scarcely be to the interests of the Government not only to cut down its valuable camphor forests, but to lose money in doing so.

If it is further taken into consideration that in the settled districts of Formosa camphor trees are scarce, that the exploitation of the forests in the savage districts is difficult, and finally that the old, primitive, and wasteful methods of manufacture are becoming more and more expensive, it would appear that the competitive power of Japanese camphor is not really so great as might be expected from its present low prices.”

The average production of Japanese Camphor during the last few years was 60000000 kin (1 kin = 0,6 kilo) of which about 80% comes from Formosa and 20% from Old-Japan. The data given below refer, it is true, only to the small share of Old-Japan (unless the contrary is especially stated), but they may nevertheless be of interest in view of the inferences which may be drawn from them for the entire production.

Under the influence of the high prices ruling for camphor it was formerly the aim of the Monopoly to increase the output by all available means. For this reason the purchasing prices per 100 kin were advanced in February 1906 by 5 to 7 yen (1 yen = 2.10 m.) and again, in April 1907, by a similar amount. Since the last-named date, therefore, the producers have obtained from 65 to 68 yen per 100 kin.

In addition to this the afforestation of those camphor districts which were being exhausted was stimulated energetically, with the result that by March 1909 about 19000 acres had been planted with 28000000 young trees.

But the Monopoly was forced to recognise that since the advent of the artificial German camphor and the revival of the Chinese production it was no longer in a position to dictate the terms. After refraining from selling for a considerable time it decided to make concessions in prices, and since September 1908 it has been selling in Japan at the rate of 78 to 80 yen per 100 kin, and in London and New York, since the autumn of 1908, at 135/- to 140/- per cwt. It has also ceased to stimulate the production, and in March 1909 it lowered the price at which it buys from the producers by 8 to 9 yen per 100 kin. But the latter, who had foreseen this reduction, exerted themselves as much as possible and in the Financial Year 1908 they succeeded in supplying to the Government, at good prices, larger quantities than it had received since the establishment of the Monopoly in 1903.

In order to diminish the losses suffered by the Monopoly at its low selling prices the utmost economy was practised and the expenses were kept down as much as possible. This is the reason why in September 1908 a new regulation was introduced, under which part of the camphor oil was sold to refiners, and the camphor obtained from it repurchased. Previously it had been the custom to supply the refiners with oil simply on condition that the camphor separated from it (equal to about one-half of the oil) was returned to the Government, the residue of the refining process, consisting of red and white oil, and of tar, being the refiners' compensation for their work.

The following table gives particulars of the production of camphor and camphor oil, the purchasing prices paid for them by the Monopoly, and the percentage of foreign bodies in the camphor. The table covers the whole period of the existence of the Monopoly.

Year and Material		Kin	Percentage of water and other foreign bodies	Cost-price Yen
1903	Camphor	371504	7,66	186509
	Camphor oil	434314	—	116968
1904	Camphor	633792	8,86	330043
	Camphor oil	714367	—	202189
1905	Camphor	600085	7,27	329916
	Camphor oil	652556	—	189417
1906	Camphor	734625	6,79	436281
	Camphor oil	850464	—	264847
1907	Camphor	746729	7,49	474605
	Camphor oil	959316	—	316356
1908	Camphor	826367	6,02	517723
	Camphor oil	1023903	—	333756
	Oil-camphor	492356	4,92	158761

The following statistics give particulars of the results obtained in the refining of camphor oil. The great loss in weight during the process is especially noticeable.

	1903 Kin	1904 Kin	1905 Kin	1906 Kin	1907 Kin	1908 Kin
Refined camphor oil . . .	443 919	733 966	661 774	865 992	964 826	1024 373
Yield of:						
Separated camphor . . .	230 258	374 559	340 952	432 639	482 165	492 356
Red oil	86 600	143 870	130 657	169 928	187 016	201 769
White oil	68 791	114 428	104 026	135 943	152 924	183 261
Tar	88 78	147 66	133 65	17 328	19 481	13 999
Total	394 527	647 623	589 000	755 838	841 586	891 385
Loss of weight in refining .	49 392	86 343	72 774	110 154	123 240	132 988

The loss in weight of the camphor while it is in the hands of the Monopoly is fairly important. After the camphor has been delivered at the Monopoly stations, about 1,5% volatilises in the course of transportation and storage. Much larger still is the loss in weight during the manipulation of working-up, which consists either in simply keeping the camphor in the warehouse up to nine months, in order to allow the oil run out (Crude camphor B.), or in distillation, by which the degree of purity of the camphor is increased to 97% (Crude camphor A. or improved B.).

The following table gives particulars of the quantity of material used in working-up the finished article to a condition ready for sale and of the remaining semi-manufactured article.

Year	Quality	Crude Material				Product finished Kin	Semi-manuf. product Kin
		Crude camphor Kin	Oil-camphor Kin	Semi-man. mat. Kin	Total Kin		
1908	Improved B B	258 656 569 232	470 583 —	46 213 —	775 452 569 232	657 262 545 703	3 610 5 246
	Total	827 888	470 583	46 213	1344 684	1202 965	8856
1907		599 746	446 758	17 941	1064 445	915 641	16 213
1906		726 970	421 626	19 077	1167 673	1031 120	17 941
1905		593 647	334 086	48 612	976 345	829 145	19 077
1904		612 322	373 103	87 279	1072 704	878 230	48 612
1903		320 501	188 692	—	509 193	360 000	87 279

The next table shows the quantity sold, the returns from sales, the total expenses, and the profit and loss of the Monopoly in Japan Proper (Old-Japan).

Year	Quantity of camphor sold Kin	Returns from sales Yen	Expenses Yen	Profit or loss Yen
1903	360 000	279 610	303 473	— 23 863
1904	878 050	726 186	601 777	+ 124 409
1905	829 200	753 876	593 848	+ 160 028
1906	1 031 100	1 173 622	772 523	+ 401 099
1907	787 200	901 519	863 398	+ 38 121
1908	503 304	441 336	1 089 007 over	— 600 000

In Formosa, owing to the lesser cost of production, the conditions are much more favourable, as will be seen from the following figures relating to the working of the Monopoly in that island.

Year	Quantity of camphor sold Kin	Returns from sales Yen	Expenses Yen	Profit or loss Yen
1903	4 292 049	3 198 778 8 784	1 734 787	+ 1 472 775
1904	4 520 521	3 688 938 21 145	1 790 922	+ 1 919 161
1905	3 709 875	3 296 704 14 034	1 692 558	+ 1 618 180
1906	4 039 504	4 570 047 33 153	2 339 808	+ 2 263 392
1907	—	4 812 712	2 872 662	+ 1 940 050

It should, however, be noticed that no detailed returns concerning the Formosa Monopoly for 1907 are yet available and that the figures given above may therefore possibly include the value of the unsold stock, for which reason it is impossible to draw any definite conclusions from the figures showing the alleged profit of 1 940 050 yen. If we compare the figures for Japan Proper, showing a considerable diminution of profit in 1907 as compared with the previous year, it is probable that the real profit made in Formosa in 1907 was much smaller than the sum mentioned above.

The column "Returns from sales" contains double sets of figures. The upper figures indicate the main revenue and those below (as, for instance, 8 784 for the year 1903) signify the revenue from the sale of by-products, such as safrol and "disinfectol".

Up to the present only small quantities of camphor have been consumed in Japan itself. There are now, however, in course of erection two celluloid works with a proposed annual capacity of over 2 000 000 lbs. It remains to be seen whether with the opening of these works, of the future of which nothing definite is yet known, the camphor consumption in Japan will increase.

The table below gives particulars of the quantities and values of the total exports of camphor from Japan and Formosa as shown by the Customs Statistics of the last ten years.

Year	Quantity Kin	Value Yen	Year	Quantity Kin	Value Yen
1900	4 851 915	4 456 345	1905	4 527 794	4 619 160
1901	5 037 989	4 694 263	1906	4 833 981	5 855 514
1902	6 996 299	6 253 964	1907	5 322 457	7 646 001
1903	6 724 176	6 056 149	1908	3 478 565	3 773 903
1904	5 544 257	5 367 517	1909		
			(Jan. 1 to Oct. 31)	7 257 482	6 312 245

The principal buyers were the U. S. America, France, U. K., Germany, and British India.

The exports of camphor from Foochow in 1908 only amounted to 9644 cwts., of a value of £ 69302, against 23231 cwts., value £271433, in 1907. The average value per cwt. declined from £ 13.15.0 to £ 7.3.9. The reasons for this remarkably heavy fall are said to be the slump in the price of Formosa camphor and the competition of the synthetic preparation. Especially striking was the reduction in the exports of camphor oil, from 10345 cwts., value £ 20805, in 1907 to 99 cwts., value £ 119, in 1908¹).

In spite of the fact that the condition of the camphor market is everywhere regarded as unsatisfactory, a native merchant named Liu, who is connected with one of the richest Chinese traders in Formosa, proposes to exploit the vast camphor forests in the Chinese provinces of Hupeh and Hunan, and to bring the product on the market *via* Hankow. The camphor which has so far been shipped from this port (1906: 372 piculs, value 18600 H. T.; 1907: 1300 piculs, value 78300 H. T.; 1908: 213 piculs, value 11408 H. T.) was transit-merchandise from Sze-chwan, a province in the Interior of the Empire²).

Cayla³), in the course of a report on the present position of the camphor-market, refers to experiments made by Campbell and Eaton at the Botanical Gardens at Batu-Tiga, Selangor, in preparing camphor from leaves. The plants were raised from Japanese seed, sown in May 1904, and were transplanted in December 1904. When 5 years old the plants were in excellent condition, most of them being 20 and some even 27 feet high. The leaves from these trees were dried partly entire and partly cut-up, and distilled moist, as were the twigs, which had been cut up into one-inch pieces. It was shown that the drying of the leaves (provided it be not done in bright sunlight), does not affect the yield of camphor, a conclusion which agrees with that arrived at some time ago by Giglioli⁴). The distillate from the leaves consisted mainly of camphor, with only a small proportion of oil; the yield was considerably larger than that obtained from the twigs and the wood from the trunk, being, in fact, equal to at least 1 % of the fresh green leaves.

In consequence of these favourable results the separate parts of the camphor-tree; leaves, twigs of less than $\frac{1}{2}$ " thickness, thicker branches, trunk, and root were subjected to comparative distillation-

¹) Diplomatic and Consular Reports No. 4379, p. 5, November 1909.

²) Chem. Industrie 32 (1909), 521.

³) Journ. d'Agriculture tropicale 10 (1910), 8.

⁴) Comp. Report April 1909, 24.

tests. The yield of camphor obtained from the various parts was as follows: —

Leaves	1 0/0
Twigs	0,216 0/0
Thicker branches and trunk	0,662 0/0
Root	1,20 0/0.

It follows that in the case of young trees the leaves afford the best distilling-material, as the roots, of course, are not available for use. Three hours is a sufficient time for distilling the leaves and twigs (it is not stated for what quantity). In Formosa it is usual to continue the distillation of the chopped wood for 24 hours.

Seed and seedlings of Japanese origin which had been put in the ground at Kuala-Lumpur in September 1907 had grown up in 18 months' time into trees 5'4" high, of which the leaves contained 0,6 0/0 camphor. Experiments are also being made in Kuala-Lumpur with Borneo camphor-trees, of which several nine-year old specimens are available.

The leaves and young shoots of camphor-trees planted in Jamaica contained only 0,23 0/0 camphor and 0,28 0/0 oil. In Antigua the plants yielded only oil to the extent of 1,2 0/0 from the herbaceous parts and 0,4 0/0 from the wood.

Cayla reiterates his previous statements that the future of camphor-production lies in the utilisation of the leaves.

Cananga Oil. Shipments of this article have not been very plentiful, but they were sufficient to satisfy the current demand. We are most particular in the selection of the oil we buy, and we supply an article of exquisite quality, far above the ordinary commercial brands. The value of the oil during the past few months has remained unchanged with a firm feeling and the quotations continue to be worthy of attention.

Caraway Oil. Very little that is definite can at present be said about the prospects of this article. The area under caraway is everywhere larger than it was in 1909, but it is, of course, possible that much of it will be ploughed up if the spring-weather should be favourable for sowing. In the province of Groningen the fields look excellent. In the Northern part of North Holland, as well as in Brabant and Zeeland they are good, but in the Haarlem Lake the outlook is bad. In any case, however, there is for the present no reason for anticipating unfavourable results, as has been suggested in certain quarters in order to cause a demand for the article. A moderate quantity of old stock is still available, but it is mainly in the hands of well-to-do farmers who are no longer, as they used to be, under the necessity of disposing of their holdings in order to provide cash. For this reason

the prices were able to maintain themselves throughout the winter. Best average quality is still worth from 16 to 16.50 fl. per 50 kilos, while for seed of the 1910 crop, August-September delivery, 15.75 fl. has been asked and paid. It is therefore probable that during the next few months the prices of caraway oil will remain unchanged.

Cardamom Oil. An American periodical¹⁾ contains information on the culture of cardamoms in Ceylon, from which it appears that the plants thrive best at an altitude of from 2000 to 3000 feet, presuming that they are sufficiently sheltered from wind and sun. The fruit is gathered before they are fully ripe and is cleaned, bleached, and dried, after which it is ready for export. The cardamoms are pale-yellow and the natives like to chew them, as they impart a pleasant odour to the breath. The plants are increased either by dividing the rhizome or from seed. During the three years following the laying down of a plantation the yield is but slight, but after 6 years an annual crop equalling from 250 to 500 lbs. per acre may be looked for. The plants bear all through the year, and the fruit is gathered once every two or three weeks; it is, however, not pulled off, but cut by scissors. The Malabarcardamom plants differ from the Ceylon plants by the leaves being softly pubescent on the under-side and by the flowers being nearer to the ground. The latter peculiarity is by no means agreeable to the planters, because in consequence it leads to the fruit being easily damaged. The Mysore cardamom plants do not show this drawback. They also differ from the others in having the leaves glabrous on both sides.

Oil of Carrot seed. Until recently very little was known of the composition of this oil, which is the distillate of the fruit of the carrot (*Daucus Carota* L., N. O. Umbelliferæ). Landsberg²⁾ surmised that it contained pinene, and in the fractions with a boiling point exceeding 200° he observed an oxygenated body $C_{10}H_{18}O$, but of this he was unable to ascertain the nature. E. Richter³⁾ has recently examined an oil of wild carrot, supplied by our firm, which he found to possess the following constants: $d_{15}^{20} 0,9439$, $n_{D15}^{20} — 2,53^{\circ}$ (in a 2 cm tube), $[\alpha]_{D15}^{20} — 13,38^{\circ}$, acid no. 2,04, ester no. 18,22, ester no. after acetylation 69,97; readily soluble in the usual organic solvents⁴⁾. Among its separate constituents the following were determined: butyric acid (probably isobutyric acid) and palmitic acid, in the ester-form, also free

¹⁾ Oil, Paint & Drug Reporter 76 (1909) No. 12, p. 28 D.

²⁾ Arch. der Pharm. 228 (1890), 25; Gildemeister and Hoffmann, *The Volatile Oils*, p. 583.

³⁾ Arch. der Pharm. 247 (1909), 391, 401.

⁴⁾ In our Report October 1907, 31, we quoted the constants of some oils distilled by us.

acetic and formic acids. From the lævogyrate portions of the saponified oil, which boiled between 150 and 160° , Richter isolated a fraction with b. p. 158 to 166° ($d_{14}^{\circ} 0,8633$; $\alpha_{D15}^{\circ} - 8,45^{\circ}$) in which he proved the presence of pinene by means of the nitrosochloride and the nitrolbenzylamine. The latter body possessed the same m. p. as a preparation obtained from d-pinene ($[\alpha]_D + 2,94^{\circ}$), from which fact Richter concludes that the pinene of oil of carrot seed is also d-pinene, an erroneous inference, because, as is well-known, d- and l-pinene yield the same inactive nitrolbenzylamine. So far as the determination of active pinene is concerned, it must be borne in mind that pinenes with a high rotatory power are unable to form nitrosochlorides. In a fraction boiling at from 168 to 176° ($d_{14}^{\circ} 0,8624$; $\alpha_{D15}^{\circ} - 5,85^{\circ}$) the author discovered l-limonene, which he identified more closely from the nitrosochloride and the nitrolpiperidine (m. p. 103 to 106°). The portion with a high boiling-point contained a crystalline body $C_{15}H_{26}O_2$, which Richter calls Daucol, and which he regards as a divalent sesquiterpene alcohol. This body, when purified by way of its xanthogen compound, forms white needle crystals with a silky lustre, m. p. 115 to 116° ($[\alpha]_{D14}^{\circ} - 17,15$ to $17,47^{\circ}$). When acetyled, only one acetyl-group reacted although the presence of two atoms of oxygen points to the existence of two hydroxylgroups. No bromine was absorbed.

Shortly before this Report closed for press, Deussen¹⁾ published a paper in which he discusses at length Richter's discovery of pinene in oil of wild carrot. Deussen concludes that this pinene is not d-pinene, as is asserted by Richter, but l-pinene. Deussen also complains that the literary references as to the preparation of pinene-nitrosochloride and nitrolamine do not refer to the pinene compounds, but to the limonene compounds.

Cassia Oil. The cassia oil market has only undergone slight fluctuations during the winter, the quotations ranging from $3/6$ to $3/4$. This slight improvement is probably due, at any rate for the greater part, to the fluctuations in the rate of exchange of silver in China rather than to supply and demand. Oil of high percentage is naturally the most in demand and we regard it as a gratifying result of the efforts we have made for many years past that oils of low percentage appear gradually to be losing all their interest for buyers.

The U. S. Bureau of Manufactures has recently published a somewhat extensive report by the Consul-General in Canton, in reply to a circular posted by the American Government asking for information on the production of cassia and cassia oil in the Far East. We have already dealt with this subject in considerable detail in our Report

¹⁾ Berl. Berichte **43** (1910), 523.

for October 1895, on which occasion we gave particulars of a journey in the cassia oil districts, which a well-known firm in Hong Kong had caused to be undertaken at the time. The report of the Consul-General, however, gives some new information which we desire to lay before our readers, although it contains several inaccuracies throwing a doubt upon the value of the whole work. It is stated that the propagation of the trees is undertaken under the auspices of some sort of a nursery-garden and that the plants, as soon as they are a few inches high, are planted out on the slopes of the hills where they are left to themselves without care or manure. In the course of six or seven years they grow to a height of seven or eight feet, the trunk measuring five inches in diameter. Then, between April and June, they are cut down to the root, and the stump covered with earth. In the course of six years the tree has again attained its former height and is then once more treated in the same manner. The life of a plant of this kind is about thirty years. From the trunk *cassia lignea* is prepared, while the branches and leaves, as well as the bark which falls off, are employed for distilling cassia oil. Next follows the description of a cassia oil distilling plant, which need not be referred to here, because it chiefly agrees with that published by us, with the well-known illustration, in our Report of April 1893. It is said that every separate distillation takes six days and nights and that the exhausted material is used for heating the stills. The annual exports from the provinces of Kwang-si and Kwang-tung, where the oil is produced, vary from 200000 to 266000 lbs. In 1907 the exports from the whole of China are said to have amounted to 1576800 lbs. to the value of \$ 560444 gold, most of which was sent out via Hong Kong. It is worth mentioning that the American Government has also addressed its circular on cassia oil to its consuls in Tonquin, Indo-China, Java and Ceylon and has ascertained that in these countries cassia oil is not produced (*sic!*).

Perrot and Eberhardt¹⁾ have published a botanical and economic study on the cinnamon trees of Indo-China. In those regions the cinnamon tree is scarcely ever cultivated, the drug being invariably obtained from wild trees. It is commercially divided into three classes, the bark from the central portion of the trunk furnishing the most esteemed quality, that from the lower part of the trunk and from the larger branches being the next best, and the third or lowest quality consisting of the thin bark from the branches. It is the intention to bring this last grade upon the European market. The supply of bark

¹⁾ Bulletin des Sciences pharmacologiques 16 (1909), 1. From a reprint kindly sent to us.

from the wild trees of Indo-China, however, is insufficient for local and Chinese requirements. The authors show that the cinnamon of Annam and Tonquin is not derived from *Cinnamomum Loureirii* Nees but from *C. obtusifolium* Nees, from which it follows that the other kinds must be regarded as varieties, that is to say, Chinese cinnamon or cassia bark as *C. obtusifolium* var. *Cassia* (Bl.) Perrot et Eberhardt and Cochin China cinnamon as *C. obtusifolium* var. *Loureirii* (Nees) Perrot et Eberhardt. We are only able to make a passing reference here to the anatomical and histological details of the branches and leaves of *Cinnamomum obtusifolium* Nees which are described, and pictorially illustrated, by the authors.

Cultivated Chinese cinnamon (of which the wild parent-plant is unknown,) possesses, it is true, a few special characteristics, but according to Perrot and Eberhardt these are insufficient to warrant us in regarding this tree as a separate species. With respect to Cochin China cinnamon the authors make a few reservations, as their experimental material was insufficient.

The possibility of a profitable cultivation of the cinnamon above described must be kept in view, but it cannot be definitely predicted whether such cultivation would really be very remunerative.

Cedar-wood Oil is suffering from enormous over-production especially in the United States. The fact that in spite of this the importance of our own manufacture has very greatly increased, affords sufficient proof of the great differences in quality which are met with in this oil, an article of such great importance in the manufacture of toilet-soaps. It also shows that our preparation has the preference over the cheap American oil, which latter usually carries with it the mark of a primitive mode of manufacture in the form of its acrid odour. The condensed variety of oil which we prepare for optical purposes is one of our specialities and has become indispensable to all manufacturers of optical instruments and requisites.

Celery Oil. It is well-known that oil of celery seed consists mainly of terpenes¹⁾. About 18 years ago²⁾ we traced, by means of the tetrabromide, the presence of d-limonene in the oil. The fractions with a high b. p. to which the oil owes its characteristic odour, form only an insignificant proportion of the whole. Ciamician and Silber³⁾, in a series of admirable investigations, discovered in the fractions with high boiling points the following compounds, viz., sedanolide, sedanonic acid anhydride, two phenols, a hydrocarbon $C_{15}H_{24}$ and palmitic acid.

¹⁾ Gildemeister and Hoffmann, *The Volatile Oils*, p. 546.

²⁾ Report April 1892, 15.

³⁾ Berl. Berichte **30** (1897), 492, 501, 1419, 1424, 1427; Report October 1897, 15.

While engaged in preparing sedanolide and sedanonic acid from the oil, we took the opportunity of examining in detail the remaining constituents. We were also interested in ascertaining in what proportions the various constituents are present in the oil, for all previous examinations had only been made with first runnings or with the residues of distillation.

The oil examined by us, which was of our own distilling, possessed the following constants: d_{15° 0,8946, $a_D + 67^\circ 51'$, n_{D20° 1,48566. When distilled *in vacuo* about 60 % passed over at the boiling point of the terpenes, then followed an intermediate fraction of about 3 %, after which about 15 % passed over between 110° and 130° (9 mm.) and 8 % between 175° and 202° (9 mm.). The residue of distillation was 10 %.

The bulk of the hydrocarbons boiled between 175° and 180° . No constituents were present with b. p. below 173° . The action of bromine produced from all fractions (d_{15° 0,843 to 0,848; $a_D + 99^\circ 50'$ to $99^\circ 15'$) a plentiful yield of the tetrabromide of d-limonene, the fraction $[\alpha]_D + 118,4^\circ$ giving the most abundant output. From the high power of optical rotation and the rich tetrabromide yield of all fractions it is probable that these fractions consist almost entirely of d-limonene.

The alcohol fraction, b. p. 195° to 230° , amounted to from 12 to 15 g. Owing to the scarcity of material available, and because this fraction apparently consisted of a mixture of various alcohols, it was not further examined.

The fraction which boiled between 110° and 130° (9 mm.), and which weighed about 60 g., consisted for the greater part of a sesquiterpene. This sesquiterpene proved to be identical with none of the known sesquiterpene-hydrocarbons, for which reason we gave it the name of selinene (from τὸ σέλινον = celery). Ciamician and Silber¹⁾ had already, while examining the residue of distillation of celery oil, called attention to the occurrence of a hydrocarbon $C_{15}H_{24}$, b. p. 262° to 269° , but these two investigators gave no further particulars respecting this body. But it is certainly highly probable that the selinene which was found by us to form the principal constituent of the sesquiterpene fraction of celery oil is the same hydrocarbon which was discovered by Ciamician and Silber in their distillation residue.

No uniform product could be obtained by fractionation from the portion with a b. p. between 110° and 130° (9 mm.), a small proportion of phenols which still remained in this fraction preventing this. In order to remove these phenols the fractions were shaken up several times with 5 % soda liquor and the hydrocarbon removed from

¹⁾ Berl. Berichte **30** (1897), 496.

the solution distilled over sodium. It now passed over between 2 and 273°. The constants of the body obtained by this method were as follows: —

1st fraction. B. p. 120 to 121° (6 mm.), $d_{17,5^\circ}$ 0,9197, $\alpha_D + 35^\circ$ 1, n_{D21° 1,49863.

2nd fraction. B. p. 121 to 122° (6 mm.), d_{18° 0,9170, $\alpha_D + 38^\circ$ 1, n_{D21° 1,4956.

The sesquiterpene, or rather mixture of sesquiterpenes, constituted a yellow liquid of an agreeable odour, which did not solidify even when cooled down considerably.

By passing hydrochloric acid into the ethereal solution of the hydrocarbon we obtained an ample yield of a solid chloride, which, after evaporation of the ether, crystallised out in needles from the reddish blue residue. The crystallising-process of the chloride was materially facilitated by a slight addition of alcohol and the application of a freezing mixture. The product, after being crystallised once, melted at 68 to 70°. The m. p. of a sample which had been repeatedly recrystallised from methyl alcohol was found to be 72 to 74°.

0,2456 g. subst.: 0,2510 g. AgCl.

Found	Calc. for $C_{15}H_{24} \cdot HCl$	$C_{15}H_{24} \cdot 2HCl$	$C_{15}H_{24} \cdot 3HCl$
Cl 25,14%	14,76%	25,63%	34,63%

The chloride was optically active in the same direction as the hydrocarbon. A sample which had been recrystallised once, m. p. 68 to 70° gave in a 10,79 per cent. ethereal solution a rotation of $+ 0^\circ 35'$, which corresponds to a specific rotation of $[\alpha]_D + 7^\circ 32'$. The highest rotation observed in a sample which had been repeatedly purified was $+ 0^\circ 57'$ in a 4,07 per cent. chloroform solution, corresponding to a specific rotation of $[\alpha]_D + 18^\circ$.

By splitting off hydrochloric acid with sodium ethylate a hydrocarbon possessing the following properties was recovered from the chloride: — B. p. 268 to 272° (the bulk 268°), d_{15° 0,9232, d_{20° 0,9196, $[\alpha]_D + 49^\circ 30'$, n_{D20° 1,50483, mol. refr. found 65,82, calculated for $C_{15}H_{24/2}$ 66,15. The hydrocarbon which was obtained from the dihydrochloride is again converted by means of hydrochloric acid in ethereal solution into the dihydrochloride, m. p. 72 to 74°.

It is therefore possible to obtain the hydrocarbon in the pure state by means of the dihydrochloride, that is to say, insofar as it is at all possible, in view of the possible formation of isomerides, to regenerate a hydrocarbon from a chloride.

So far, all efforts to obtain from the hydrocarbon a nitrosite, nitrosate or nitrosochloride have been unsuccessful, but as soon as a sufficient quantity of the hydrocarbon is again available we propose to continue our experiments in this direction. In any case, the fact

disclosed up to the present indicate that in selinene we have a new hydrocarbon of which the occurrence in essential oils was previously unknown, and which can be readily identified by its constants and by its dihydrochloride. Its properties very closely resemble those of cadinene, but it may be easily distinguished from the latter by its lower boiling point and the different melting point of its dihydrochloride.

Those fractions of celery oil with the highest boiling points which have been examined by us were found to contain the constituents already described by Ciamician and Silber. Phenols only occurred in small proportions, and their further examination was not possible. We succeeded in isolating, from the fractions in question, sedanolide and sedanonic acid anhydride by the methods followed by the Italian investigators. From 491 g. oil we only obtained 34 g. of a mixture of sedanolide and sedanonic acid, but we were able to isolate 2 g. of pure sedanonic acid (m. p. 107 to 109°; under rapid heating 111 to 113°), and 13 g. of pure sedanolide, of which the b. p. was found to be 163° (5 mm.). (Ciamician and Silber give it as 185° [17 mm.]).

The research, therefore, has yielded the following results: — Oil of celery consists of not less than 70% hydrocarbons; that is to say, of 60% d-limonene and about 10% d-selinene, a bicyclic sesquiterpene not previously observed in essential oils. Alcohols are present in the oil to the extent of from 2,5 to 3%. From the portions with a high b. p. which had already been examined by Ciamician and Silber we succeeded in isolating from 2,5 to 3% of pure sedanolide and 0,5% sedanonic acid anhydride.

Cinnamon Oil, Ceylon. This article has enjoyed a very active demand and its manufacture in our works is steadily extending. In the year 1909 we distilled over 100000 kilos of Ceylon cinnamon chips, while our sales exceeded in quantity even those of the year 1908. It is, of course, a fact that the quality of our oil is beyond all praise. The imports of cinnamon chips *via* Hamburg have again increased somewhat during the past year, when they amounted to 2941578 lbs., against 2785824 lbs. in 1908.

On a previous occasion we have reported on cinnamon bark oil from the Seychelles Islands¹⁾ and in continuation of this report we subsequently stated²⁾ that the cinnamon trees in the Seychelles were originally introduced from Ceylon. Rosenthaler³⁾ has now examined a sample of the bark, supplied to him by us, and has ascertained in the first place that the bark differed from all other cinnamon barks known

¹⁾ Report November 1908, 41.

²⁾ Report April 1909, 33.

³⁾ Berichte d. deutsch. pharm. Ges. 19 (1909), 490.

and described. Recently Rosenthaler has procured young examination material from Mahé, and in conjunction with Reis he has continued his investigations on bark from the branches and trunk. Anatomically the structure of the branch-bark agrees entirely with that of Ceylon cinnamon. The authors give a precise, illustrated description of the bark from the trunk. As this bark was derived from the same tree which produced the branch-bark it follows that it, too, must be Ceylon cinnamon. According to Rosenthaler and Reis the differences in the constitution of Ceylon and Seychelles cinnamon oil which have been observed by us, do not apply to the question of origin, because in the matter at issue the bark is of different age and geographical origin.

The authors give the following analysis showing the chemical constitution of the bark from the trunk:

Aqueous extract	6,52 %
Alcoholic extract	7,27 %
Total ethereal extract	4,20 %
Volatile ethereal extract	2,83 %
Non-volatile ditto	1,37 %
Protein matter	2,04 %
Crude fibre	36,04 %
Cinnamic aldehyde	1,33 %
Water	9,38 %
Ash	8,6 %
Sand (parts of the ash insoluble in HCl)	0,44 %
Sand-free dry matter	90,19 %
Sand-free ash of the sand-free dry matter	9,05 %

Citronella Oil. The shipments of Ceylon citronella oil from Galle in the year 1909 reached the record, totalling not less than 1512084 lbs., that is to say about 235000 lbs. more than in the previous year. The excess in shipments took place chiefly during the summer-months and had as a result that the prices receded to nearly 11 d. per lb. The forecast of the course of the market in this article which we gave in our October Report, has therefore proved true. At the present moment (beginning of March) the reports are that the market is rather slack at a value of 11½ d. cif.

The supplies during the time under review occasionally left much to be desired in the matter of quality. This led to several claims in London, in the settlement of which our opinion was invited. It would lead us too far to enter into details on the matter here and it will be sufficient to record the fact that as a result of these claims the question of the introduction of a more stringent test to take the place of our "Schimmels Test", which, though it has proved its usefulness, no longer meets the present needs, has again become a matter of importance.

In Java citronella oil the offers far exceed the requirements. It appears that the plantations have again been increased out of all proportion, and it is therefore not surprising that over-production, from which the article suffered some years ago, is again making itself felt. Consumers, who of course will be able to take advantage from this position, will be glad of an opportunity of buying this popular and useful oil at exceptionally favourable terms for some time to come.

Several years ago we showed that Java citronella oil contains citronellal, geraniol and d-citronellol.¹⁾ We were also able to prove the presence in the oil of methoxylgroups, which points to the occurrence of methyleugenol, a body which had already been found by us in Ceylon citronella oil.²⁾ So far, no further constituents had been made known, but we have recently succeeded in isolating a previously unknown constituent from Java citronella oil, to wit, citral. From a large quantity of Java citronella oil which had a clearly perceptible odour of citral, a small fraction was redistilled repeatedly, and the fraction distilling over between 98 and 100° (7 mm.) (d_{15}° 0,8836; $\alpha_D - 1^{\circ}30'$) treated with neutral sodium bisulphite by the familiar process for the purpose of separating the citral. This body, after being regenerated and distilled *in vacuo*, gave the following constants, which agree closely with those of pure citral from lemongrass oil: b. p. 91 to 92° (5 mm.), d_{15}° 0,8928, $\alpha_D \pm 0^{\circ}$, n_{D20}° 1,48853, m. p. of the naphthocinchonic acid 197 to 198°. It should be stated that the citral content of Java citronella oil is but small, being computed at about 0,2%.

We were able, last year, to give some particulars of a citronella oil³⁾ from German New Guinea which had been submitted to us for consideration. Recently we received a similar oil from our German Colonies in the Southern Pacific, and this sample was found to possess the following constants: — d_{15}° 0,8964, $\alpha_D - 1^{\circ}20'$, geraniol and citronellal content 78%, soluble in its own volume and over of 80 per cent. alcohol. Although this oil also resembles the Java oil in its general characteristics, its geraniol content is rather less, and falls below that of the sample examined last year by about 8%.

The previously existing regulations for the testing of citronella oil having proved insufficient, the Saxon Customs and Excise Authorities have decided to abolish definite regulations for the examination of the oil altogether, and, (as in the case of rosemary oil, *q. v.*) to leave to

¹⁾ Report April 1900, 13; April 1902, 20.

²⁾ Report October 1899, 22.

³⁾ Report April 1909, 37.

the chemists entrusted with the work a free hand in respect of methods to be applied in determining the value of the oil. In order, however, to afford some guide to the examiners, there has been issued together with the official announcement, a communication giving the results obtained in the examination of Ceylon citronella oil at the Imperial Technical Testing-Office in Berlin. I reproduce these results in full: —

Colour and odour. Great weight is to be attached to both of these, since from the colour and odour of an oil it is possible to obtain a good indication of the adulterants for which search should be made in a particular instance. For example: water-white samples with a pronounced odour of camphor have been met with which were found to consist of mixtures of fusel oil and camphor oil with bodies which have not been further investigated, and in the case of these samples it was doubtful whether they contained any citronella oil at all. Citronella oil often has a green colour, resulting from contact with copper in the process of manufacture. Where the copper has not been removed by shaking with dilute aqueous solutions of acids the oil generally has a brown colour, which readily turns green on exposure to air¹). The agreeable and very persistent odour of the oil is often, but inappropriately, described as "balm-like". It is altogether *sui generis*, and from this fact is highly indicative of citronella oil.

The determination of sp. gr. is only useful for the detection of gross adulteration with petroleum and other hydrocarbons. The commercial variety described as "Singapore oil" has a sp. gr. of 0,886 to 0,900, but oil of the "finest" quality scarcely enters into consideration for denaturing-purposes. The great bulk of the oil of commerce, known as "Lana Batu", has a sp. gr. of 0,900 to 0,920. The addition of petroleum lowers the density, but such an addition must be considerable before it can be detected absolutely by this factor.

The test for solubility in alcohol serves for the detection of petroleum or of fixed oils. Citronella oil which has been adulterated with a not too large proportion of petroleum gives a clear solution with from 1 to 2 volumes of alcohol, (*i. e.*, 80 per cent. alcohol,) when further diluted the solution turns milky, and when it is left to stand for some time drops separate out on the surface. Where the adulterant is a fixed oil, dilution with an equal volume of alcohol is sufficient to produce turbidity and when the sample is left to stand the fixed oil settles in drops at the bottom.

It is only the formation of drops which affords a certain clue to adulterations of this nature, inasmuch as "pure" commercial oils may also turn turbid. The test for total geraniol is of great importance in

¹) A brown colour would point to the presence of iron.

judging of the purity of the oil. The joint geraniol and citronellal content of the oil is determined by acetylation. But this determination also may be affected by certain additions, such as fusel oil. It is therefore desirable to note the odour of the acetic esters which are formed in the course of this manipulation. Samples examined in this Bureau which were adulterated with fusel oil, when acetylated, had a clearly perceptible odour of amyl acetate. This odour differs unmistakably from those of the geraniol acetate and of the *isopulegol* acetate formed from citronellal.

The optical rotation, which ranges from -20 to 3° , also affords a hint to the purity of the oil, but this constant, of course, is also liable to be influenced by adulterants.

The fractional distillation 30 cc. of oil in a Ladenburg flask (comp. Gildemeister and Hoffmann, *The Volatile Oils*, p. 190), also gives valuable clues. Pure Ceylon citronella oil, under this treatment, behaved as follows: —

190 to 218°	. . .	5 cc.
218 „ 231°	. . .	5 „
231 „ 239°	. . .	5 „
239 „ 249°	. . .	5 „
249 „ 264°	. . .	5 „ , decomposition commences.

In two cases where citronella oil had been adulterated with camphor oil and fusel oil, the first indication thereof in the testing-process was that considerable proportions passed over below 190° . In the fractional distillation of 100 g. of oil part of the fraction was separated. It had the unmistakable odour, and approximately the b. p., of amyl alcohol. From the fractions with the higher b. p. a sufficient quantity of camphor was separated to make it positively identifiable by its m. p. and that of its semicarbazide.

For the rest, it must be left to the chemist concerned to the test to the special requirements of the case.

*The Perfumery and Essential Oil Record*¹⁾, a periodical which has recently been started by J. C. Umney, contains a short criticism of the solubilitytest for citronella oil which was introduced by us (Schimmel's Test). The criticism chiefly amounts to a suggestion for the improvement of our test by adding to it the requirement of a minimum content of geraniol (60%).

The point of view expressed in this criticism is quite in accord with our opinion that the content of total geraniol is the first factor in determining the value of citronella oil. Besides, Umney²⁾ and Parry

¹⁾ *Perfumery and Essential Oil Record* 1 (1910), 4.

²⁾ *Chemist and Druggist* 48 (1896), 356; *Report* April 1896, 18.

and Bennett¹⁾ made similar proposals years ago, their demand, at that time, being for a minimum of 58% of total geraniol. There would therefore scarcely appear to be differences of opinion with regard to the justification for such a demand; on the contrary, the desire to combat more energetically than heretofore the malpractices of sophistication by setting up more stringent tests, will express itself with increasing keenness as time goes on.

For this reason we proposed, now several years ago, a more stringent form of "Schimmel's Test", "Raised Schimmel's Test"²⁾, as follows: —

"Citronella oil, to which has been added 5% of Russian petroleum should give a clear solution at 20° C. with 1 to 2 volumes of 80 per cent alcohol. This solution, even after the addition of ten volumes of the solvent, should remain clear or at most show a feeble opalescence. In any case, even after a considerable time has elapsed, no drops of oil should separate out."

We are certain that if this more stringent or "raised" form of our Test had been generally applied in commerce, it would soon have been followed by a considerable general improvement in the quality of the oil. Unfortunately the test has not been so applied, possibly because it was feared that, if it were, many pure oils would be excluded, seeing that it was occasionally asserted that pure oils sometimes failed to stand even the ordinary Schimmel's Test³⁾. This assertion is undoubtedly without foundation, nor is it to be feared that pure oils in normal condition would be unable to stand the severer test; in fact, not a single valid reason can be adduced for such a contention. In our own investigations we have always found that oils of really good quality do stand the more stringent form of examination, and we therefore now once more urge the introduction of this "raised" test.

It is true, of course, that a solubility-test of this kind has only a restricted value, and can only afford general data as to the quality of an oil, but it has this advantage, that it can be applied easily by any person without special technical knowledge.

Altogether different conditions would arise if the geraniol determination, which is of incomparably greater importance in the estimation of citronella oil, were introduced, for its execution requires a certain experience which only trained chemists can be presumed to possess. This fact would naturally cause initial difficulties, yet in the interest of the subject it would be desirable if a method were discovered which would enable the total geraniol determination to be carried

¹⁾ Chemist and Druggist 62 (1903), 999; Report October 1903, 26.

²⁾ Report April 1904, 32.

³⁾ Report October 1903, 26; April 1906, 19.

out generally. The best plan of all would be if the Government of Ceylon were to superintend the citronella oil business on the spot, as, according to statements made some time ago¹⁾, appeared to be its intention. The oils ought to be tested by Government chemists and should only be allowed to be exported if they contained at least 80% totalgeraniol, and if in other respects also they conformed entirely to the tests prescribed. An official certificate to this effect should be given with each parcel of oil tested and the exportation of all oils *without exception* which failed to answer the test should be prohibited. We should regard it as a mistake if any relaxations were to be made, and oils of less than the standard quality were also to be admitted for exportation, as was the intention of the Ceylon Government in the year 1904. The rigorous enforcement of such a regulation would probably be attended by the best results, as it would mean a final removal of the evil and would once more turn the citronella oil trade into healthy channels.

The proposal which is made by Parry²⁾ in a lengthy article on Ceylon citronella oil also deserves careful attention. He suggests that dealings in the oil should simply be made on the basis of its content of totalgeraniol, in the manner which has long been applied with success to cassia oil and lemongrass oil in respect of their aldehyde content. By establishing this principle, each oil would be sold according to its intrinsic value, and there would then be very little object in adulterating it. Parry gives the content of total geraniol of the best Ceylon oils as from 77 to 83%.

In connection with this matter, Parry also refers to Schimmel's Raised Test, but in the course of his statements he makes the mistake of declaring that the oil, when diluted with 10% of petroleum, should be tested for solubility in 80 per cent. alcohol. This statement requires correction to the meaning that the oil, when 5% of Russian petroleum has been added to it, should pass the ordinary test.

According to A. J. Ultée³⁾ several oil-yielding grasses, especially *Cymbopogon Nardus*, *C. citratus*, *C. Martini*, and *Vetiveria zizanioides*⁴⁾, are grown in the Botanical gardens at Salatiga (S. E. of Buitenzorg, Java). The most important of these is *C. Nardus*, or citronella grass. As the altitude of Salatiga is considerably above that of Buitenzorg, Ultée made experiments for the purpose of ascertaining whether this difference influences the character of the oils. He obtained by distillation 0,66% of an almost colourless oil with the following constants:

¹⁾ The Ceylon Observer, 16. Aug. 1904; Report October 1904, 19.

²⁾ Americ. Perfumer 4 (1910), 211.

³⁾ Cultuurgids, Orgaan van het Algemeen-Proefstation op Java 11 (1909), 404.

⁴⁾ Comp. Report April 1907, 30.

$d_{290} 0,8721$, $\alpha_D - 3^\circ 15'$, totalgeraniol (calculated by de Jong's method) 92,75%, soluble in 1,5 vols. and more of 80 per cent. alcohol. The oil was distinguishable from the Buitenzorg distillates in the first place by its greater solubility, for according to de Jong the Buitenzorg oil only gave a clear solution with 3 vols. of 80 per cent. alcohol, which became cloudy when diluted to over 4 vols. As Ultée only obtained an oil yield of 0,66%, whereas in Buitenzorg the yield ranged from 0,5 to 0,9%, experiments were made at Salatiga to ascertain whether the oil content of the grass could be raised by suitable fertilizing. Of four experimental fields, three were treated for this purpose with differently-composed artificial manures. The grass was cut after 10 weeks and equal quantities of it distilled in an exactly similar manner. The oil yields obtained ranged from 0,60 to 0,65%, showing that manuring had not affected the oil content of the grass.

Clove Oil. It has always been a difficult and ungrateful task to report on the clove market, for it is notorious that in doing so one has to rely upon data supplied by persons whose interests are very divergent and who in most cases, it might almost be said invariably, contradict each other on material points. Thus, our estimate of the 1909/10 crop given in our last Report has proved to be too high. In one quarter the output has recently been stated at 110 000 bales and in another at 70 to 75 000 bales. It is therefore probable that in reality it is somewhere between 80 and 90 000 bales. In sympathy with this result the prices of cloves have moved in an upward direction until reaching lately their present level of about 56.— m. per 50 kilos. For the present the movement appears to have been arrested and it will depend, as usual, in the first place upon the attitude of the speculators whether or not a further rise will ensue. In Hamburg the remaining available stocks are small, for the greater part of the supply of about 2000 bales, which was warehoused there at the end of last year, has in the meantime gone into consumption without the stocks being replenished by new arrivals. It is said that at the beginning of March the stock in London was about 47 250 and in Rotterdam and Amsterdam about 20 000 bales.

In clove-stems an upward movement of prices set in in January because a manufacturer of clove oil in Hamburg thought it advisable to cover his requirements for the current year. As a result the quotations advanced in a short time from about 14.— m. per 50 kilos to about 17.— m. For the present it is impossible to form any definite opinion as to the future of this important article. The import of clove-stems in Hamburg in 1909 amounted to about 1 300 000 kilos that is to say, not less than double the quantity of 1908. The fact

¹⁾ Comp. Report April 1909, 36.

that in spite of this enormous supply the prices could be maintained in the course of the past year shows how extraordinarily large is the consumption of oil from clove stems, which, as is well known, is chiefly used in the manufacture of vanillin.

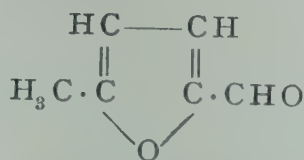
A sample of clove oil which was recently received by us, showed the cunning manner in which oils are sometimes adulterated. The oil was expressly said to have been distilled from cloves. We determined the constants as follows: d_{15° 1,0488, $\alpha_D - 4^\circ 58'$, phenol content 70%, soluble in 1,3 vol. of 70 per cent. alcohol; when more alcohol was added, cloudiness ensued. Although the specific gravity and the just sufficient phenol content of the oil did not at first give rise to suspicion, the high opt. rot. and the very deficient degree of solubility nevertheless aroused a doubt. A more thorough investigation showed that the isolated phenols contained, besides eugenol, impurities with an odour reminding of creasote, while the portions which were freed from phenol contained an abundant quantity of safrol; products which, of course, do not occur in natural oil of cloves and which could only have been present as adulterants. The oil in question was evidently simply an artificial concoction, made up principally by the aid of suitable camphoroil fractions.

R. Reich¹⁾ has worked out a method for the direct estimation of essential oil and eugenol in cloves. He distils the cloves with steam, saturates the distillate with common salt and extracts it with a liquid of low b. p. (such as ether or rhigolene), weighing the residual oil after evaporating the solvent. For a description of the apparatus employed for distillation we refer to the original paper, but it may here be observed in passing that the powdered cloves are mixed with particles of pumice-stone, placed in a cartridge surrounded by a steam-jacket, exposed to the current of steam and distilled to exhaustion. According to Reich, $1\frac{1}{2}$ to 2 hours are required to complete the distillation of 10 g. cloves, and from 600 to 800 cc. of distillate must be collected. The distillate saturated with common salt is extracted three times, each time with from 25 to 30 cc. rhigolene (pentane), a body which has the advantage of not absorbing water. The solvent is then evaporated. The author points out that not all essential oils are miscible with pentane in any proportion; therefore when the method is employed to estimate essential oils other than clove oil, it is necessary to determine by experiment which particular solvent is the most suited to the special purpose in view. By this method, the estimation of the essential oil content of the various spices can be accomplished in from 6 to 8 hours.

¹⁾ Zeitschr. Untersuch. der Nahrungs- u. Genussmittel 18 (1909), 401.

For the determination of the eugenol content of clove oil Re gives the following *modus operandi*: From 1,0 to 1,5 g oil are saponified for a quarter of an hour with 20 cc. 5 per cent. soda solution in a condensing tube in a water bath, with frequent shaking. The mixture is then left to cool, 20 cc. petroleum ether with a low b. p. is added and the whole shaken up vigorously. The clear petroleumether solution is removed, the eugenol-sodium solution placed into a shaking-cylinder and its volume increased to 30 cc. by the addition of more 5 per cent. soda solution. Of the completely bright solution, 15 cc. is then placed into a second shaking-cylinder, 5 cc. 5 per cent. sulphuric acid, 6 g. common salt and 20 cc. pentane are added, and the mixture shaken up continuously. As soon as the aqueous and the pentane solution have become separated from each other, and formed two perfectly clear layers an aliquot part (15 cc.) of the pentane solution is pipetted into a Mann weighing flask and when the solvent has evaporated the residue is weighed.

H. Masson¹⁾ describes a series of newly-discovered constituents of clove oil. From the fractions with b. p. 50 to 75° (15 mm.) he isolated by treatment with phthalic acid anhydride a mixture of alcohols, which he ascertained the presence of methyl-n-amylcarbinol (heptanol-2), $\text{CH}_3\text{CH}(\text{OH})(\text{CH}_2)_4\text{CH}_3$ (b. p. 157 to 158°; $d_{20}^\circ 0,8344$) and of furfuralcohol (b. p. 170 to 171°; $d_{20}^\circ 1,1615$; m. p. of the diphenylurethane 97,5°). The methyl-n-amylcarbinol was further identified by oxidising it into methyl-n-amylketone (b. p. 151 to 152°). In the fractions possessing a b. p. of 75 to 100° (15 mm.) the author ascertained the presence of methyl-n-heptylcarbinol (nonanol-2), $\text{CH}_3\text{CHOH}(\text{CH}_2)_6\text{CH}_3$ (b. p. 195 to 196°; $d_{20}^\circ 0,8399$), and benzylalcohol (b. p. 206°; $d_{20}^\circ 1,0627$), which he identified by oxidising them into methyl-n-heptylketone, and benzoic acid respectively. Masson further found an unsaturated alcohol (methylfurfuralcohol?). In addition to methyl-n-heptylketone, which had already been discovered by us in oil of cloves²⁾ the fractions of which the b. p. lay between 65 and 95 (15 mm.) contained α -methylfurfural: b. p. 184 to 186° (at normal press.), 75° (20 mm.), $d_{20}^\circ 1,1365$.



α -Methylfurfural.

The last-named body was identified from the semicarbazone (m. p. 210 to 211°), the phenylhydrazone (m. p. 147 to 148°) and by ox-

¹⁾ Compt. rend. **149** (1909), 630, 795.

²⁾ Report April **1903**, 27.

ation to α -methyl pyromucic acid (m. p. 107 to 108°). The fractions with a b. p. of from 105 to 120° (15 mm.) contain a dimethylated surfurol (b. p. 206 to 208°), which, when oxidised, yields a pyromucic acid melting between 129 and 130° , but the position of the methyl-groups could not be determined. The author also demonstrated without doubt the presence, in these fractions, of methyl salicylate, the existence of which in oil of cloves had not yet been proved with sufficient certainty.

Copaiva Balsam Oil, Pará. In this oil a lack of supply was occasionally noticeable, but we always succeeded at the right moment in discovering material suitable for distilling. Prices, however, have lightened by a few marks per kilo and appear inclined to remain at this level. It should be noted that this oil has lately been used to a somewhat considerable extent in the paint industry.

Coriander Oil. As we had foreseen, the supplies of coriander seed of the 1909 crop were insufficient, Russian seed being the only variety available, and we were only able to distil a limited quantity ourselves. Fortunately, considerable quantities of oil from the previous season remained at our disposal and the increases in price which took place in the course of the last few months were therefore confined within certain limits. Until the new crop is ready for working, a decided scarcity must certainly be expected, and there is no doubt that in the course of the summer the quotations will reach a very considerable height, particularly so because it is doubtful whether the cultivation of coriander seed will again be taken up in Moravia and Hungary. Thuringian seed has long ceased to be a factor in the preparation of essential oil.

Oil of *Cryptomeria japonica*. Some years ago this oil was examined by Kimoto¹⁾ and by Keimatsu²⁾. Kimoto found in the oil a body $C_{30}H_{48}O$, to which he gave the name of sugiol; while Keimatsu observed a sesquiterpene differing from cadinene, which he called cryptene. More recently, H. Kimura³⁾ has investigated an oil of cryptomeria which he had himself obtained from the wood to an extent of about 1,5 p. c. by means of steam distillation. This oil had a yellow colour and possessed the following constants: $d_{20} 0,9453$, $[\alpha]_D - 23^\circ 1'$, acid no. 0, ester no. 3,88. The principal portion boils between 150 and 160° (17 mm.) and contains cadinene, which was identified by the hydrogen chloride compound (m. p. 117 to 118°), as well as another sesquiterpene which yields only liquid additive products when treated with hydro-

¹⁾ Bull. Coll. Agric. (Tokio) **4**, 403; Report October **1902**, 32.

²⁾ Journ. of the Pharm. Soc. of Japan **1905**, 189; Report April **1906**, 23.

³⁾ Berichte d. deutsch. pharm. Ges. **19** (1909), 369.

chloric acid gas, and to which the author has given the name "suginene". Regenerated from the hydrogen chloride compound "suginene" gave the following constants: $d_{0,918}$, $[\alpha]_D - 10^\circ 34'$. This is also present in the oil a sesquiterpene alcohol which, when regenerated from the potassium compound, possesses the following properties: b. p. 163° (10 mm.), $d_{0,964}$, $[\alpha]_D - 37^\circ 5'$. This body Kimura calls "cryptomeriol". In the process of purification over the xanthogen compound this body appears to be converted into an alcohol melting at 135 to 136°, to which the name of *isocryptomeriol* was given. The oil is said to contain about 40% alcohols and 60% sesquiterpenes. It is asserted that old oils are richer in alcohol than recent samples.

Cubeb Oil. The arrivals of cubebs in Europe are falling more and more, because the consumption in the United States has increased considerably and better prices are obtainable there than here. As a result the market has advanced enormously and it has been necessary more than once to increase the quotations of genuine oil by several marks per kilo. It does not appear that there is any prospect of a decline in the values within a reasonable time.

Cumin Oil. Remains unchanged with a weak demand.

Cypress Oil. As is well known, the distillation of Italian cypress leaves and branches is one of our particular specialities and we are therefore able to guarantee in every respect the quality of the oil we supply. Unfortunately the popularity enjoyed by this excellent remedy for whooping-cough, which was introduced by us, has had as its sequence that from other quarters, and especially from France, cypress oils have been placed upon the market of which the efficacy is open to considerable doubt, because they appear not to be derived from *Cupressus sempervirens*. We therefore again seize this opportunity to utter a strong warning against "cheap" qualities. It is not surprising that during the winter-months the call upon our stocks has been very heavy; we believe, however, that we shall have sufficient until the present year's distilling material is available in July and August.

In our Report for October 1904¹⁾ we stated in the course of a note on cypress oil that the only difference between cypress camphor with m. p. 86 to 87° and dextrorotatory cedar camphor was the optical inactivity²⁾ of the former. At the same time we mentioned that, when subjected to the action of formic acid, cypress camphor yielded a dextrorotatory, and cedar camphor a laevorotatory, hydro-

¹⁾ Report October 1904, 25.

²⁾ Also compare Gildemeister and Hoffmann, *The Volatile Oils*, p. 269.

carbon. Both these statements, so far as they relate to cypress camphor, require correction inasmuch as recently, on the occasion of working up a considerable quantity of material, it was shown that cypress camphor as well as cedar camphor is dextrorotatory, and, like the other, is converted into a lævorotatory hydrocarbon $C_{15}H_{24}$ by dehydrating agents. The opt. rot. of this hydrocarbon was found to be $-85^{\circ}57'$. A solution of 2 g. cypress camphor (six times recrystallised) in 20 cc. chloroform, gave $\alpha_D + 2^{\circ}1'$ in a 200 mm. tube. This works out at $[\alpha]_D + 10^{\circ}5'$. The value for cedar camphor observed at the time was $[\alpha]_D + 9^{\circ}31'$ (in 11.2 % chloroform solution). Cedar camphor and cypress camphor must therefore be regarded as identical.

Dill Oil. From Galicia we received some time ago a sample of dill oil which was suspicious on account of its too high sp. gr. ($d_{15^{\circ}} 0.9425$) coupled with a too slight optical rotation ($\alpha_D + 48^{\circ}16'$) as well as by its high refractive index ($n_{D20^{\circ}} 1.50775$). Its solubility in 80 per cent. alcohol also left something to be desired, as the solution did not become quite clear. Our first impression was that the oil had been distilled from the herb, but this was abandoned by the absence of phellandrene in the oil, and subsequent examination showed the oil to have been grossly adulterated. The presence of liberal proportions of anethol showed without doubt that the adulterant was oil of fennel.

Essential Oils, Sicilian and Calabrian.

We have to express our thanks to Mr. Eduardo Jacob of Catania for having supplied us with the subjoined report: —

A glance at the statistics for 1908 (page 48) shows that the exports not only reached those of 1907 but surpassed them by 2413 kilos, which leaves us face to face with the fact that the world's consumption in the course of the year 1906 amounted to a total quantity of 950000 kilos in round figures, and that during the two years 1907—8 1050000 kilos annually have been taken out of the market.

From this it appears that the annual requirements of the world range from 950000 to 1050000 kilos. This estimate is confirmed by the average figures for the last decade, which amount to 934952 kilos for the period 1899 to 1908. The earthquake of December 28th 1908 has occasioned some changes in the statistics for the year 1909, in so far as concerns the directions in which the essential oil trade of Sicily and Calabria had moved up to that time. Apart from the fact that the destruction of the two cities of Messina and Reggio compelled the majority of the exporters to transfer the scene of their activity from those cities to Catania and Palermo, it would seem that the venturesome proceedings in the principal consuming centres caused

users all over the world, shortly after the earthquake, to practise extraordinary degree of caution. The result of this was that through the year 1909 consumers were apparently unable to bring themselves to buy more than they absolutely required.

It can only be attributed to fear and anxiety on the part of buyers abroad that the exports in 1909 only reached 604299 kilos showing a decrease of 455012 kilos as compared with the preceding year, and of 330653 kilos as compared with the average of the 10 years. On the other hand these figures prove that the oil-supply abroad have been consumed everywhere, down to the smallest centre in which the trade penetrates, and are urgently in need of ample replenishment. This view is supported by the heavy shipments of the first months of the present year and by the numerous demands from abroad which are being steadily received in this market.

So far, the prospects for the new crop may be described as very favourable. In contrast to the severe winter of 1908/9 the weather this year has been chiefly fine and mild, with few storms; the verdure of the trees is therefore magnificent, and this is a necessary condition for rich blossoming and a subsequent good harvest. If the favourable outlook should be realised during the spring months, it is probable that the result will make itself felt in a corresponding manner in the market-prices of our oils during the late summer.

Comparative exports of essential oils in 1907 and 1908.

Destination	1907		1908	
	kilos	lire	kilos	lire
a) from Messina:				
North German Ports	21 299	489 877	24 263	485 26
Austria-Hungary	61 301	1 409 923	73 716	1 474 32
Belgium	2 899	66 677	3 524	70 48
Denmark	2 140	49 220	3 492	69 84
France	31 710	729 330	31 926	638 52
Greece	276	6 348	470	940
U. K.	213 811	4 917 653	242 670	4 853 40
Netherlands	10 119	232 737	8 674	173 48
Russia	8 855	203 665	10 505	210 10
Sweden	3 635	83 605	4 418	88 36
Norway	3 550	81 650	4 845	96 90
Spain and Portugal	4 678	107 594	3 861	77 22
Turkey	1 223	28 129	1 492	29 84
U. S. America	483 705	11 125 215	388 380	7 767 60
South America	—	—	898	17 96
Australia	33 993	781 839	51 244	1 024 88
Egypt	1 623	37 329	1 621	32 42
India	581	13 363	2 053	41 06
Italy	19 037	437 851	17 670	353 40
Other countries	2 066	47 518	4 031	80 62
Total	906 501	20 849 523	879 753	17 595 06

Destination	1907		1908	
	kilos	lire	kilos	lire
b) from Catania:				
North German Ports	—	—	1 000	20 000
Austria-Hungary	1 136	26 128	3 812	76 240
Belgium	—	—	300	6 000
France	—	—	57	1 140
U. K.	283	6 509	545	10 900
U. S. America	—	—	300	6 000
Other countries	671	15 433	—	—
Total	2 090	48 070	6 014	120 280

c) from Reggio:				
North German Ports	3 548	81 604	4 024	80 480
Austria-Hungary	31 346	720 958	38 500	770 000
France	35 811	823 653	40 327	806 540
U. K.	25 807	593 561	38 030	760 600
Netherlands	2 320	53 360	1 450	29 000
U. S. America	32 062	737 426	40 771	815 420
Other countries	460	10 580	933	18 660
Total	131 354	3 021 142	164 035	3 280 700

d) from Palermo:				
North German Ports	800	12 000	—	—
Austria-Hungary	1 080	16 200	600	9 000
France	1 272	19 080	690	10 350
U. K.	11 910	178 650	7 883	118 245
U. S. America	1 510	22 650	150	2 250
Other countries	381	5 715	186	2 790
Total	16 953	254 295	9 509	142 635

Comparative total exports in 1907 and 1908.

Port of shipment	1907		1908	
	kilos	lire	kilos	lire
Messina	906 501	20 849 523	879 753	17 595 060
Catania	2 090	48 070	6 014	120 280
Reggio (Cal.)	131 354	3 021 142	164 035	3 280 700
Palermo	16 953	254 295	9 509	142 635
Total	1 056 898	24 173 030	1 059 311	21 138 675

As compared with 1907, the exports of 1908 show an increase in weight of **2413 kilos**, but a decrease in value of **3034355 lire**.

Comparative exports of essential oils in 1908 and 1909

Destination	1908		1909	
	kilos	lire	kilos	lire

a) from Messina:

North German Ports	24 263	485 260	2 673	53 4
Austria-Hungary	737 16	1 474 320	8 340	166 8
Belgium	3 524	70 480	440	8 8
Denmark	3 492	69 840	1 133	22 6
France	31 926	638 520	8 549	170 9
Greece	470	9 400	—	—
U. K.	242 670	4 853 400	54 555	1 091 10
Netherlands	8 674	173 480	420	8 4
Russia	10 505	210 100	1 019	20 3
Sweden	4 418	88 360	1 049	20 9
Norway	4 845	96 900	280	5 6
Spain and Portugal	3 861	77 220	70	1 4
Turkey	1 492	29 840	47	9 4
U. S. America	388 380	7 767 600	30 706	614 12
South America	898	17 960	—	—
Australia	51 244	1 024 880	550	11 00
Egypt	1 621	32 420	40	8 0
India	2 053	41 060	335	67 0
Italy	17 670	353 400	2 161	43 22
Other countries	4 031	80 620	280	5 60
Total	879 753	17 595 060	112 647	2 252 94

b) from Catania:

North German Ports	1 000	20 000	15 672	313 44
Austria-Hungary	3 812	76 240	42 980	859 60
Belgium	300	6 000	6 510	130 20
Denmark	—	—	413	8 26
France	57	1 140	13 076	261 52
Greece	—	—	—	—
U. K.	545	10 900	48 193	963 86
Netherlands	—	—	4 869	97 38
Russia	—	—	1 397	27 94
Sweden	—	—	341	68 2
Norway	—	—	—	—
Spain and Portugal	—	—	—	—
Turkey	—	—	55	1 10
U. S. America	—	—	1 520	30 40
South America	300	6 000	196 276	3 925 52
Australia	—	—	1 320	26 40
Egypt	—	—	1 223	24 46
India	—	—	73	1 46
Italy	—	—	—	—
Other countries	—	—	—	—
Total	6 014	120 280	334 158	6 683 10

Destination	1908		1909	
	kilos	lire	kilos	lire
c) from Palermo:				
North German Ports	—	—	3913	58695
Austria-Hungary	600	9000	6565	98475
Belgium	—	—	180	2700
Denmark	—	—	280	4200
France	690	10350	11609	174135
Greece	—	—	170	2550
U. K.	7883	118245	41911	628665
Netherlands	—	—	870	13050
Russia	—	—	429	6435
Sweden	—	—	—	—
Norway	—	—	—	—
Spain and Portugal	—	—	1390	20850
Turkey	—	—	30	450
U. S. America	150	2250	10237	153555
South America	—	—	433	6495
Australia	—	—	3599	53985
Egypt	—	—	195	2925
India	—	—	—	—
Italy	—	—	45	675
Other countries	186	2790	25	375
Total	9509	142635	81881	1228215

d) from Reggio:				
North German Ports	4024	80480	435	8700
Austria-Hungary	38500	770000	12235	244700
France	40327	806540	28584	571680
U. K.	38030	760600	10523	210460
Netherlands	1450	29000	—	—
U. S. America	40771	815420	23352	467040
Other countries	933	18660	484	9680
Total	164035	3280700	75613	1512260

Comparative total exports in 1908 and 1909.

Port of shipment	1908		1909	
	kilos	lire	kilos	lire
Messina	879753	17595060	112647	2252940
Catania	6014	120280	334158	6683160
Reggio (Cal.)	164035	3280700	75613	1512260
Palermo	9509	142635	81881	1228215
Total	1059311	21138675	604299	11676575

These figures show a decline in the exports in 1909, as compared with 1908, of 455012 kilos and 9462100 lire.

Table showing the exports of the last ten years.
1899 to 1908.

Year	kilos	lire	Year	kilos	lire
1908	1059311	21138675	1903	864770	1196483
1907	1056898	24173030	1902	1085497	1519693
1906	948328	18556053	1901	820982	1231473
1905	868244	13709760	1900	842246	1097229
1904	1006103	14758590	1899	797145	1072244

Average of the last ten years: —

934952 kilos, value 15350737 lire.

There have been slight differences in the physico-chemical constants of oils of bergamot and lemon as compared with last year. The bergamot oil produced this year up to the latter end of January was of a very low ester content, the average probably not exceeding 36%, and only those oils which were produced later had a higher ester content, which, however, did not come up to the high estimates of the previous year. At the beginning of the production season the rotatory power of the lemon oil was normal; but the weather caused the lemons still remaining on the trees to ripen more quickly than usual, as a result of which the majority of the districts are already yielding oils of which the rotation ranges from 57 to 59, and no doubt the rotatory power will be reduced still further.

Taking the different varieties of essences in detail, it may be stated that no favourable expectations were entertained of the result of the new **Bergamot** crop. The high prices of this oil which ruled throughout the year 1909 had induced consumers to practise economy in the use of the article and to endeavour to replace it in part by other oils or artificial compounds, with the result that some supplies of bergamot oil from the year 1909 were carried forward to the next season. These, however, were unable to supply the deficiency of the new crop which was foreseen and has actually occurred. An estimate placing the production of bergamot oil during the current year about 40% below that of the previous year is probably close to the truth, especially when it is considered that there was not only less fruit but also that the oil content of the individual fruit was smaller.

The low oil content of the fruit contributed to aggravate the position of the manufacturers, who, apart from this circumstance, had been compelled to pay very high prices owing to the poor prospects of the crop and who were further faced with a serious shortage of labour and consequent rise in wages.

In these circumstances it is not surprising that the cost of the oil to the manufacturers was much in excess of their original estimate.

and this explains the tenacity with which they held their supplies, parting with them only when they were able to command prices which were in unison with the high cost of production. Before the beginning of the new crop bergamot oil was sold for delivery at about 28.— marks, but in the course of December and January the exporters were compelled to fall in with the demands of the holders and to pay figures up to a parity of 36.— marks per kilo. When the oil had reached the last-named price, manufacturers began to show an increased tendency to sell, and the excessive rise was followed by a natural reaction, foreign buyers temporarily holding back from the market, so as to bring about a state of things in which they should be able to supply their demands, in so far as they were still uncovered, at moderate prices. If we take into consideration that a very small output of oil has taken place, it is to be assumed that there is scarcely any prospect of much lower prices than those now prevailing, and that within the next 9 months there may easily occur times at which the requirements of foreign buyers may give a fresh upward impetus to the prices of this oil in our market.

The preparation of oil is now at an end in almost all districts, but at present it is impossible to form a correct estimate of the existing supplies.

Lemon Oil. The new lemon crop is generally estimated at from 20 to 25% below its predecessor. At the beginning of the new manufacturing season, however, at least 70 to 80000 kilos of the old crop remained to swell the new season's supplies. As a result of the stock which remained over in the producing country from last year, and under the pressure of needy manufacturers who sold new oil for delivery at very low prices in order to obtain cash advances, a brisk speculative business developed at Catania in the course of the autumn, by which the majority of the exporters were tempted to sell for abroad large quantities of new oil for delivery in 1910 at lower prices than were actually obtainable in the market. During the second half of the year 1909, oil for immediate shipment was constantly being sold for abroad at the parity of 6.50 to 7.— marks, while at the same time large transactions took place for delivery during 1910 at 5.25 to 5.75 marks.

In the new season, however, the course of prices has developed in a manner totally different from that which had been expected by the bold speculators.

As we have already stated in detail in previous Reports, the proprietors of lemon gardens, in order to obtain particularly remunerative prices for their fruit, had succeeded in inducing the Government to come to the aid of the agricultural interest, which had been represented as being in danger. As is well known, only a portion of the lemons

grown in Italy can be brought upon the markets of the world in the shape of fresh fruit. One reason of this fact is that the lemon plantations which have been laid down within the last 20 years in California and Florida have almost entirely freed the United States from its previous dependency for this fruit upon Italy and Spain, with the result that the production of lemons in Europe has gradually become larger than the requirements of European consumers. Another reason is, that as a result of time and excessive cultivation the lemon trees have become subject to an increasing number of diseases which render the lemons unfit for shipment in cases. It has therefore become necessary to find another use for fruit of inferior quality, from the peel of which essential oil is now pressed, while the juice is either concentrated or made into citrate of lime, the raw material for the preparation of citric acid.

The number of works anywhere manufacturing citric acid is very small, and so, consequently, is the number of firms which are engaged here in this trade. When the steady increase in the production of lemons in America practically closed that market to the Sicilian article — a measure which has recently been confirmed by the imposition of a still higher import duty upon European lemons in the United States — the loss of this great consuming centre naturally reacted upon Europe by causing over-production. The European markets being only able to absorb a certain proportion of the annual output, the surplus of lemons was utilised in increasing quantities for the production of essential oil and citrate of lime, and this fact made itself felt in the market-prices of both products. The more ignorant class of lemon growers in Sicily, when brought face to face with the gradual shrinkage in their means of livelihood, were unable to form a clear judgment of the causes underlying this depreciation, and are possibly still unable to do so. They accused the exporters of citrate of lime of having made common cause against them with the foreign manufacturers of citric acid for the purpose of artificially depressing the value of the article.

The Italian Government allowed itself to be deceived and passed a law under which citrate of lime ceased to be an open market-article, and by which its exports were regulated by a *Camera Agrumaria* which was empowered to levy a high transit-duty upon any supplies of the article which were exported otherwise than through its intermediary. The *Camera* was also given the right to fix the selling-price of citrate of lime for six months, and of making an advance of $\frac{2}{10}$ of the value of citrate of lime deposited with it, issuing warrants for the merchandise. The object of the last-named clause was to enable the manufacturers to obtain the advances which they had previously been in the habit of receiving from the exporters, and by means of which they carried on their business.

As, however, the depreciation of lemons was really due to over-production, and not to the machinations of which the exporters and consumers of citrate of lime had been accused, the inevitable results soon made themselves felt. The high prices fixed by the *Camera Agrumaria* contributed on the one hand to decrease the consumption abroad, and on the other to increase the production of citrate of lime in Southern Italy; hence, at the close of the season 1909 there was in the warehouses of the *Camera* an unsold stock of about 6000 tons of citrate of lime, which is equal to the consumption of the whole world for about 15 months. This fact opened the eyes of many previous supporters of the monopoly, and although many may still continue to deceive themselves with false hopes, the Bank of Sicily — which had made the advances through the *Camera Agrumaria* — came to see that to continue this policy would mean the locking-up of many more millions of money for an indefinite time. For this reason the Bank refused to make any further advances on the new season's citrate of lime and urgently demanded repayment of the 8000000 lire which had already been sunk in the article.

The lengthy explanation given above is necessary in order to explain to some extent the course of prices of oil of lemon during the new season. The refusal of the Bank of Sicily to lend any more money on citrate of lime and the consequent cessation of advances upon the citrate deposited with the *Camera Agrumaria* placed all the manufacturers in the greatest embarrassment. Everyone of them had been under the belief that business would continue as before, and on the strength of this faith had entered into larger or smaller engagements for selling or buying. Then, just at the moment when the new season's work was about to commence in earnest, the means of obtaining the necessary cash in the accustomed manner suddenly ceased.

If the manufacturers had been able to obtain through the *Camera Agrumaria* further advances upon the citrate of lime produced by them, there is no doubt that the price of lemon oil would have risen at a bound immediately upon the commencement of the season. Foreign buyers of the oil, who throughout the year 1909 had only covered their most urgent requirements, entered the market at the beginning of the new crop with insistent demands, and although the acuteness of the position was somewhat lessened by the existence of old stocks, it is certain that under ordinary circumstances a wild upward-speculation would have immediately developed among the manufacturers and those allied to them, which would have driven the price of lemon oil to far above its present level. But the inability on the part of the manufacturers of obtaining cash by depositing citrate of lime with the *Camera Agrumaria* caused the market of lemon oil to take a different development.

The manufacturers who had bought lemons and who were bound to keep to the times of delivery provided for in their contracts, well as those who had already sold lemon oil for delivery, were compelled either to fail in their obligations towards the lemon-growers and the purchasers of their product by not starting work, or to obtain the necessary money somehow, and to go on manufacturing.

It should be stated to the credit of those concerned that they shrank from no sacrifices in order to fulfil their obligations as far as possible. For a few weeks it appeared as if a general strike were contemplated, with the object of putting pressure upon the Government to find fresh financial assistance, but this scheme miscarried because it was impossible to bring the many interests concerned to take common action, and in the circumstances it was left to each individual to get himself out of the mess as best he could by his own exertions.

All these negotiations of course took up much valuable time, during which it was impossible to work in the brisk manner in which it had been customary to proceed in former years. But as the only means of obtaining money which the persons concerned had at their disposal was the sale of the finished oil of lemon, the decline in production did not at first show itself on the market or cause any considerable advance in prices. The exporters who had sold large quantities of oil for delivery at the low prices of 5.25 marks and 5.75 marks referred to above, without covering themselves and on pure speculation, were under the necessity of supplying their current requirements at a loss, but if it had been possible to carry on manufacturing from the commencement in the ordinary way, their losses would have been very much heavier still.

In spite of all efforts, and with every desire to carry the manufacturing season to a successful issue, the manufacturers would nevertheless have been unable to do so if the *Camera Agrumaria* (of which the Director in the meantime had resigned and had been replaced by a Royal Commissioner), after many unsuccessful efforts, had not finally found itself able to recommence advancing money on citrate of lime.

This recommencement of advances took place in the middle of February, and its immediate result was a lessening of the offers of lemon oil on the market, because the manufacturers were no longer compelled, as before, to sell immediately every drop of the oil as they prepared it.

On the other hand, the opportunity which is now afforded to manufacturers of placing the oil in warehouse and speculating with it, has brought a multitude of speculators into the market, and as the immediate result of the re-establishment of advances on citrate of lime by the *Camera Agrumaria*, we are faced with the fact that oil of lemon

the average price of which throughout December, January and the first half of February had been from 6.75 marks to 7.— marks, has been forced up to 7.50 marks and 7.75 marks by local speculation in the course of a few days.

The present general position of the article is as follows: The season's crop shows a reduction of about 25%; a very considerable part of it — far more than in previous years — has been sent abroad in the form of cased fruit, the remainder has already gone into manufacture, or will do so within the next few weeks. The output of oil in the Eastern part of Sicily has been barely more than 65% of the quantity produced in other years, the oil content of the fruit having been extremely moderate. There is only very little available oil left in the hands of the exporters, who have had no opportunity of buying beyond their daily requirements. The supplies in the manufacturers' warehouses also are very small, being scarcely one-quarter of the average. In the Eastern part of the island manufacturing is practically at an end, and the article would certainly tend towards a very high range of prices, were it not that in the Western part of the island the manufacturing season proper is only just commencing.

The future position, therefore, depends this year solely upon the result of the oil manufactured in the Western part of Sicily. So far the fruit grown in this section of the island — where it matures later than that of the Eastern portion — had continued to find its principal market in the United States. Last year, however, the American import-duty on European lemons was considerably advanced, and no one therefore can yet foresee what shape the business in cased fruit from Palermo to the U. S. will assume this season. If the conditions of consumption and weather in the States should make it possible for the West Sicilian lemons to find a paying market there during the spring and early summer, the production of oil in that part of the island will be extremely limited and will have little weight in determining the general market conditions. But if the fruit of Western Sicily should find no market abroad in its natural state, then, in view of the fact that the crop in that part of the island must be described as satisfactory, an abundant production of oil is to be looked for, which may well serve to counterbalance the conditions in the Eastern part where the tendency is towards higher rates.

In any case, lower prices than those now prevailing may be looked upon as out of the question during the present year, while it would not be surprising if, with any increased demand from abroad, they should rise to a higher point.

It is not improbable that foreign countries will this year require more oil from our markets than in 1909, seeing that the exports during that year were excessively small.

Mandarin Oil. Mandarin oil has only been produced in limited quantities during the period under review in this report. Prices have remained unchanged.

Orange Oil, bitter. The production of bitter orange oil this year has been much less than in 1909, but the prices have undergone no great changes in the course of the last few months.

Orange Oil, sweet. The crop of oranges this season has not been very large, and owing to the high price of the fruit the quantity of oil produced has been comparatively small. Only inconsiderable quantities of oil remained over from last year at the beginning of the present season. At first the demand was very strong and caused the prices to rise by about 1.— mark in the course of the months of November, December, and January, but they fell again to the previous level during February. Last year, in order to protect the native orange-growers, the U. S. Government imposed a high import-duty upon orange oil¹). Up to the present the effect of this duty has been to restrict shipments from Sicily to America, the figures for the last 4 months having been much less than in previous years.

In Sicily the remaining stocks are very slight; in Calabria they are larger; the total supplies being very much below those of previous years at the corresponding period.

L. Trabut²), in an essay on cross-breeding in the *Citrus* species, expresses the view that the orange owes its origin to a crossing between the mandarin (*Citrus nobilis*) and the bitter orange (*Citrus bigaradia*). The author is of opinion that this cross-breeding probably occurred accidentally in a district where both varieties are cultivated. For details we refer to the original paper.

Bergamot Oil. It is well known that bergamot oil is prepared only in Calabria, and not in Sicily. For this reason an oil of bergamot may be of interest which was sent to us recently from Palermo with the statement that it had been pressed locally from the fruit of bergamot-saplings grafted on a lemon tree standing in a garden in the centre of that town. The oil did not differ from Calabrian commercial oil, and possessed the following constants: $d_{15^{\circ}}$ 0,8829, $\alpha_D + 15^{\circ} 20'$, acid no. 1,5, ester no. 100,7, equivalent to 35,2 % linalyl acetate, evaporation residue 58 %, soluble in one-half its vol. and more of 90 % alcohol. No clear solution could be obtained with 80 % alcohol.

¹) See Introduction, p. 10.

²) Compt. rend. 149 (1909), 1142.

Two samples of bergamot oil which were recently submitted to us for our opinion proved to be adulterated with terpinyl acetate. Their behaviour was as follows: —

	d_{150}	α_D	Residue of evaporation	Estercontent (Calc. as linalylacetate)
I.	0,8966	$+ 22^\circ 6'$	4,0 %	38,2 %
II.	0,8980	$+ 23^\circ 20'$	3,3 %	39,0 %

The sp. gr., which was much too high, as well as the unusually small residue of evaporation (in a pure oil these constants are respectively from 0,881 to 0,886 (15°) and from 4,75 to 6 %), at once aroused suspicions, which were confirmed when the two oils were fractionally distilled. Comparison with an undoubtedly pure oil showed that the two samples contained fractions with high b. p. such as are never met with in a pure oil. Furthermore, the rotation and refractive index of the separate fractions differed from those of the pure oil. In the case of No. I these facts appear to indicate an additional sophistication.

Behaviour on Boiling. (3 mm.)

Fraction	I.			II.			Pure Bergamot oil		
	%	α_D	n_{D20°	%	α_D	n_{D20°	%	α_D	n_{D20°
1. to 40°	2	$+ 36^\circ 35'$	1,47225	10,6	$+ 52^\circ 34'$	1,47235	18,6	$+ 58^\circ 16'$	1,47303
2. 40° „ 50°	38,8	$+ 60^\circ 5'$	1,47274	28,5	$+ 64^\circ 47'$	1,47264	18,9	$+ 68^\circ 51'$	1,47245
3. 50° „ 68°	9,1	$- 11^\circ 32'$	1,46030	3,9	$+ 8^\circ 35'$	1,46664	5,6	$+ 17^\circ 15'$	1,46545
4. 68° „ 72°							21,4	$- 15^\circ 20'$	1,45781
5. 72° „ 78°							20,2	$- 11^\circ 16'$	1,45331
6. 78° „ 82°									
7. 82° „ 88°	12,1	$- 8^\circ 56'$	1,45871	14,8	$- 6^\circ 12'$	1,45991			
8. 88° „ 91°	20,1	$- 3^\circ 42'$	1,46011	19,5	$- 2^\circ 16'$	1,46229			
9. Residue	5,4	$- 1^\circ 30'$	1,46387						
	12,5			14,0			15,3		

Fractions 6, 7 and 8 had a pronounced odour of terpinyl acetate. For the purpose of further testing they were saponified, after which the alcoholic constituents were fractionated *in vacuo*. The parts which distilled over between 75° and 80° (3 mm.) had a sp. gr. of 0,9174 (15°) and consisted chiefly of terpineol.

The examination detailed above supplied us with some interesting observations in another direction. It was found, in agreement with experiments which had been made in our laboratory some time before, that the time required for saponifying the two adulterated oils differed from that of a genuine bergamot oil. Whereas the latter could be saponified within half an hour, the result of an additional half hour's boiling of the spurious oils was a considerable rise in the ester number,

due to the well-known fact that terpinyl acetate saponifies less readily than does linalyl acetate. We submit the results obtained.

	I.		II.		Pure Bergamot oil	
	Ester no.	Ester %	Ester no.	Ester %	Ester no.	Ester %
$\frac{1}{2}$ hour's saponification . .	96,8	33,9	94,7	33,1	101,3	35,5
1 hour's saponification . . .	109,2	38,2	111,3	39,0	100,7	35,3

As linalyl acetate is completely saponified in half an hour, it follows from the above figures that not less than 4,3 and 5,9 % of terpinyl acetate respectively had been added to the two oils in question.

As we are still engaged in investigating the rate of saponification of the several esters, we reserve further communications on the subject, in the hope that we shall be able, as a result of our experiments, to establish a method for the qualitative, and possibly also the quantitative, detection of certain artificial esters.

The scarcity of bergamot oil last year, in consequence of the earthquake-disaster in Calabria, resulted in adulteration of the article upon an enormous scale. In connection with this matter, J. C. Umney¹⁾ reports on two samples of oil which, although their constants were still within the limits laid down for bergamot oil, proved upon closer investigation to be adulterated with terpinyl acetate. Umney also believes that he has ground for assuming that the oils in question contained orange oil, or the terpenes thereof, but of this he brings forward no proof. The constants of the two oils under review were as follows: d_{15}^0 0,887, $\alpha_D +19^\circ$ to $+22^\circ$, ester content 41,0 to 41,5 %, residue of evaporation 4,4 to 4,5 %. On the other hand, two other oils of the same season, and of undoubted purity, behaved as follows: — d_{15}^0 0,883, $\alpha_D +17^\circ$, ester content 40,6 to 41,5 %, residue of evaporation 5,2 %. Umney holds that all oils of bergamot with a rotation exceeding 18° are already suspect, whereas any of which the rotation is more than 20° ought to be rejected. The residue of evaporation, he thinks, should not fall below 5 %. W. H. Simmons²⁾ justly opposes Umney's conclusions, giving it as his opinion that an optical rotation of 20° by no means affords grounds for suspicion, as he himself has met with oils rotating at 24° . To this criticism, Umney³⁾ makes the rejoinder that Simmons' experience must be regarded as exceptional; his own investigations, extending over many years, showing that the rotation of most bergamot oils from ripe fruit does not exceed 20° .

¹⁾ Chemist and Druggist 75 (1909), 411.

²⁾ Ibidem 487.

³⁾ Ibidem 522.

We have ourselves in previous years, as well as in the year 1909, repeatedly come across bergamot oils (many of them from the most reliable sources), of which the rotation was between 20 and 24°, and we are therefore altogether unable to associate ourselves with Umney's assertion that such oils should be rejected.

Lemon Oil. As the result of the careful investigations which have been instituted by the U. S. Department of Agriculture in Southern Italy, two pamphlets have made their appearance dealing with the cultivation and the preparation and export of oil of lemon, citrate of lime and lemon peel¹). Although the valuable contents of these two papers lie partly outside the four corners of these Reports, they yet contain so much that is of interest to our branch of industry, that we desire briefly to refer to them here.

The lemon tree grows in almost all parts of Italy from Lombardy and Venetia in the north to Calabria and Sicily in the south, but only in the last-named two districts, as well as in the peninsula of Sorrento, are the trees used for purposes of the lemon industry, as only these districts offer the climatic conditions suitable for the development of the trees. The conditions in Southern California are equally favourable, but the number of trees there is scarcely 7 per cent. of that in Calabria and Sicily. In 1904 the total number of all *citrus* trees in Italy was about 17 000 000, including 8 000 000 lemon trees. Of this quantity Sicily has at least 6 000 000, Calabria about 1 000 000, the Peninsula of Sorrento about half a million, the rest being spread throug the remainder of the country. In the island of Sicily, which is the most important district for the lemon industry, the tree is found along the north and east coasts, but scarcely ever at any great distance in the interior; only occasionally it follows the course of the rich valleys, and grows there at altitudes up to 1000 feet.

In 1907 the crop in Sicily and Calabria was estimated at 6900 million lemons. One-third of the crop, or perhaps a little more, is worked up into oil and other products. Palermo is the chief centre for the shipment of lemon fruit, but here the oil manufacture is of less importance than in other districts. On the other hand, in those parts where the condition of the fruit does not make it advisable to export it, the oil industry grows important. The principal producing district for the latter is that of Etna²) from Catania in the south to Giardini

¹) Italian lemons and their by-products. I. G. H. Powell, *The Italian lemon industry*. II. E. M. Chace, *The by-products of the lemon in Italy*. U. S. Department of Agriculture, Bureau of Plant Industry, Washington. Bulletin N. 160, 6. October 1909.

²) Comp. map of Sicily and Calabria, to be found in our Report for April 1906, as well as in Gildemeister & Hoffmann's book *The Volatile Oils*, p. 464.

in the north. The second most important district is that of Messina which reaches from Giardini to Messina; next in order is the district of Palermo, the centre of which is the city of that name, while its limits are from Ficarazzi in the east to Partinico in the west; then follows the district of Siracusa in the south-east, comprising the country from Avola in the south to Augusta in the north; and finally the district which lies between Messina and Palermo, and of which the principal centre is Barcellona.

The small district, situated in Calabria, is only of interest because there the oil is obtained by mechanical pressure. The principal producing centres of each of the separate districts are as follows: —

1. Etna District. Catania, Acireale, Giarre (near to which is the village of Carrubba, with the largest lemon oil works in Sicily producing several 100 lbs. daily), Mascali, Fiume-freddo, and Giardini.

2. District of Messina. Santa Teresa, Roccalumera, Scaletta Zanglea, Galati, Tremestieri, Mili, Contesse, Messina and possibly also Bauso and Rometta.

3. District of Palermo. Palermo, Monreale, Ficarazzi, Partinico, Carini and Cinisi.

4. District of Syracuse. Avola, Siracusa, Floridia, Priolo, Augusta and Melilli.

5. District of Barcellona. Barcellona, Patti and Santa Agata di Miletello.

As a rule manufacturing continues from December until the end of March, very occasionally until within the month of May. In the district of Palermo only, where the pressing begins later, it frequently continues until June. In the district of Siracusa the season begins earlier, and its duration here is from about 15th October to 15th April. As already stated, all lemons which are not suitable for shipment are turned into oil. The production of oil is carried out by three different processes, known respectively as the halving method the method of dividing into three, and the machine method¹).

The halving method is that followed in the districts of the Etna, Messina, and Siracusa, as well as in Patti and St. Agata di Miletello. In this process the fruit is cut into halves, either longitudinally or crossways the former only when it is intended to make further use of the peel. The pulp is removed with a sort of spoon and the scooped-out halves of the fruit are left standing moistened with water for 4 or 5 hours or overnight, before they are further treated for oil. This is said to facilitate the pressing of oil, and to increase the yield.

¹) The following descriptions are chiefly taken from a further publication by Chace, *The manufacture of flavouring extracts*. Reprint from the Year Book of the Department of Agriculture of the U. S. A. for 1908, 337. Also compare Gildemeister & Hoffmann, *The Volatile Oils*, p. 462.

The labour used in the process described is mostly that of women and children; the former are paid 1.05 Lire to 2.10 Lire; the latter 0.25 Lire to 0.75 Lire; but the pressing of the oil is entirely done by men. While engaged at his work the presser sits on a low stool and the oil is pressed into an earthenware vessel standing in front of him, and measuring from 8 to 10 in. in height and the same in diameter. At one end of the vessel is a spout and immediately below this a small recess for catching the impurities when the oil is poured out. Across the top of the vessel is a piece of wood about one inch thick on which are 3 sponges, one flat, the second rather thicker, and the third cup-shaped, into which the operator forces the lemon peel with his right hand, while with the left he presses the sponge. The peel is then turned round a little, pressed again, and this process repeated 3 or 4 times. When the lemon peel has been cut lengthways a large round sponge is used instead of the cup shaped sponge.

According to size, ripeness, and other conditions of the fruit, from 1600 to 2200 half peels produce about 1 lb. of oil. It is said that green fruit is richer in oil than ripe fruit. Moreover, the lemons should be pressed as soon as possible after being gathered. A good workman is able to press from 2 to 3 lbs. of oil daily, for which work he is paid 2.10 Lire to 3.15 Lire.

The oil is carefully poured off, the water and the residues being left behind; the two last-named are then again separated in a cloth filter, and the residue gathered in the course of several days is put under a hand-press to remove the last particles of oil. This oil is known as "*fece*"; it is of inferior quality and less agreeable odour, and is not sold separately but is mixed with the other oil.

The method of dividing in 3 parts is that which is commonly practised in Palermo and Barcellona; almost the only difference between it and that described above is the preliminary treatment of the lemons. The peel is cut from the fruit in 3 longitudinal strips, a good deal of the pulp of the fruit being removed at the same time, while a portion of the peel remains adhering to the ends of the peeled fruit. By this method, therefore, no such perfect separation of peel and pulp is obtained as by the first-named process. No cup-shaped sponge is used for pressing, but only a large round one, which is super-imposed over the two others and against which the peel is pressed out flat. As some of the pulp adheres to the peel, as mentioned above, it is obvious that in this process a larger quantity of lemon juice and residue accumulates than by the other methods; but the oil manufactured by it has the advantage of being more easily filtered and remaining clear for a longer time. The reason of this is said to be that certain constituents held in solution in the oil, which otherwise afterwards

separate out again, are immediately coagulated by the citric acid, and thus removed from the oil.

In Palermo and Barcellona the oil which remains in the residues is not recovered by pressure, but by a primitive method of water distillation. The result is a very inferior colourless oil of a disagreeable odour, which is mixed with the pressed oil.

The *machina* is used in Calabria only, and the quantity of oil obtained by this method is less than 5% of the total. This oil has a deeper colour than that obtained by the other processes, and is said to be used only in order to impart a darker tint to pale oils. In this process about 8 lemons, as far as possible of equal circumference, are placed together in the machine between two discs, of which the lower one is fixed while the upper one is rotated by a somewhat crude mechanism, its weight pressing equally upon the lemons. The rotation of the upper disc is communicated to the lemons, which while rotating, are being scratched by suitable contrivances and thus deprived of their oil. After a fixed number of rotations lasting about 30 seconds, the machine automatically indicates the completion of the pressing by acting on a bell; the oil which has been pressed out accumulates in a container placed under the press, and that which still adheres to the lemons is absorbed with a sponge. The separation of oil and residue is carried out in the manner above described. Numerous striking illustrations contribute greatly to the understanding of the processes described.

The question of the pinene-content of oil of lemon has lately been once more the subject of animated discussion. Although it is now generally agreed to that pinene forms a natural constituent of oil of lemon¹⁾, yet opinions are divided on the point up to what proportion of pinene may be regarded as normal, and where adulteration with turpentine oil commences.

The matter has been dealt with very thoroughly by Chace, who was sent on a mission to Sicily by the U. S. Government to clear up the question by studying it on the spot. The result of his enquiry has been published in the form of a pamphlet²⁾, in which, after briefly relating the reasons which led to his mission to Sicily³⁾, Chace describes broadly the different producing districts and refers to the manner in which he collected the samples of pure oils required for his work. In this matter of collection Chace has acted with the greatest

¹⁾ Comp. Report November 1908, 63.

²⁾ *The Occurrence of Pinene in Lemon Oil*. U. S. A. Department of Agriculture, Bureau of Chemistry, Circular No. 46; 30. October 1909. From a copy kindly sent to us.

³⁾ Comp. Report April 1908, 41.

possible circumspection, and the very numerous samples of oil gathered by him possess the highest possible guarantee of absolute purity. His examinations included the determination of specific gravity, refractive index, and optical rotation, both of the original oil samples and of the first fraction of 10 % thereof distilled according to our method in a Ladenburg flask. The citral content was also ascertained colorimetrically (!) by means of magenta-sulphurous acid¹⁾, a test which, according to Chace, when carried out by an expert gives results which are correct up to 0,2 % (2)

The following figures represent the range of limits of value as ascertained by Chace in 145 samples of oil: — d_{15° 0,8557 to 0,8594, α_{D20° $+55,7$ to $+64,5^\circ$ (two samples fell below this, viz., one of $54,2^\circ$ from the Messina and one of $54,9^\circ$ from the Palermo district; one was above, viz., $66,3^\circ$ from the district of Syracuse), n_{D20° 1,4743 to 1,4758, citral content 4,1 to 7 %; the differences in rotation between the original oil samples and the initial 10 % of the distillate ranged from 1,01 to 6,17°.

The principal object of the tests, however, was to determine whether pinene could be detected in the first 10 % of the distillate. For this purpose, Chace used the process already described in our Report of November 1908²⁾, by first preparing the nitrosochloride according to Wallach's method, recrystallising the crystals thus obtained from chloroform + methyl alcohol and finally using the microscope for determining whether, in addition to the needle-shaped crystals of limonene-nitrosochloride, any crystals of the pinene-compound, which occur in the form of large flakes, could be detected. Chace's pamphlet is illustrated by several reproductions of the crystal-forms as revealed by the microscope. The test gave negative results with the whole of the authentic samples collected by the author, whereas in a large proportion of the commercial oils which were exported to the United States in 1907, and which were rejected there, pinene was detected by this method, a fact which Chace attributes to adulteration with turpentine oil. Chace is the more convinced of the correctness of his view because part of the last-named oils also showed other slight deviations from his authentic samples, for instance in their indices of refraction and their citral content. (We regard it as quite a mistake to attach any value to the latter point, in view of the inaccuracy of the methods of determination).

As to the result of his investigations, Chace formulates the dictum that all lemon oils should be rejected as adulterated in which the presence of pinene can be demonstrated by the method introduced

¹⁾ Comp. Report April 1907, 116.

²⁾ Report November 1908, 63.

by us¹⁾, distillation from a Ladenburg flask there being no difference whether or not the physical constants of the oil are normal.

J. C. Umney²⁾, in a note on Chace's pamphlet, expresses the view that it will not always be an easy matter to detect with absolute certainty a small pinene content in the first 10% of a distillate of oil of lemon, and that furthermore confusion with nitrosochlorides derived from other terpenes, but similar in appearance, might take place. The presence of pinene, he observes, can only be established with certainty by the m. p. of the nitrosochloride (103°). But we are also unable to recommend this criterion, for the melting points of the nitrosochlorides of several terpenes lie close together. In order to be quite certain it would be necessary, in our view, to prepare the nitrolamines.

Apparently, Umney has not clearly grasped the real object of Chace's investigations, for he (Umney) makes use of the occasion to discredit our method of distillation, notwithstanding that this method was the very one which Chace used in his work. It is also necessary to correct Umney's assertion that we have only admitted the occurrence of pinene in oil of lemon "somewhat reluctantly". To begin with, we had good ground for assuming that pinene is not a natural constituent of oil of lemon, as our experience at that time was based upon the examination of a large quantity of that oil³⁾. When afterwards, from our own investigations⁴⁾, we had convinced ourselves that our previous observation only in exceptional cases, applied to oil of lemon we admitted the fact without cavil. Nor would we have had any cause whatever for acting in the manner in which Umney now tries to represent us as having acted. It goes without saying that in a matter of such importance as the one under discussion we desired to be quite sure of our ground, for which reason we did not say "ditto ditto" without more ado to the pronouncement of Burgess and Child, who were the first to detect the occurrence of pinene in oil of lemon, but whose results were contradicted by our own previous observations. Surely, Mr. Umney cannot find fault with us for having acted in this manner.

In opposition to Umney we must further expressly affirm that our method of distillation continues to render excellent services in testing lemon oils. It is true that a greater difference in rotation between the original oil and the first 10% of the distillate has to be allowed than is admitted by the British and the U. S. Pharmacopœias, which lay down a maximum of 2°. We have repeatedly stated that the

¹⁾ Report October 1898, 41.

²⁾ The British and Colonial Druggist 1909, p. 447.

³⁾ Report October 1897, 26.

⁴⁾ Report April 1902, 33; October 1902, 37; November 1908, 63; October 1909, 62.

difference, in the case of pure oils, ranges up to 5° , and Chace (see above) has even found it to go up to 6.17° . Parry¹) gives from 7 to 8° as the maximum value, but this, according to our experience, is too high if the work is conducted exactly in accordance with our prescription.

In a lengthy article, Parry²) expresses himself very vigorously in opposition to the requirements set up by Chace, which he regards as altogether untenable, and in which he sees merely an attempt to justify the objections raised against large parcels of oil of lemon by the U. S. Customs Authorities in the year 1907. Although the results obtained by Chace may be correct so far as concerns the oils examined by him, it does not therefore follow, (Parry thinks,) that they would be correct when applied to all oils, inasmuch as it has long been known that the properties, and consequently the constitution, of oils of lemon are subject to certain variations in different months and years according to the prevailing climatic conditions. This, of course, also applies to the pinene content, which may sometimes be a little greater and at other times a little less. It may therefore happen on occasion that pure oils fail to stand Chace's pinene test and are on that account rejected as adulterated, and this, in the interests of trade, would be most deplorable. Taking the tables published by Chace himself, Parry points out that the oils which Chace declared to be adulterated showed a precisely similar optical behaviour as did the authentic samples, while, if turpentine had been added, the differences would certainly have been greater, unless the addition only amounted to just about 2%, a percentage which of course is much too low to be seriously considered as an adulteration.

But Parry also raises doubts with regard to the reliability of the microscopical test of the nitrosochlorides. For, according to Wallach, limonene nitrosochloride occurs in two isomeric forms which have a different crystallisation, and as by Chace's method about 80% of the one and 20% of the other form are produced, this determination, too, might easily lead to a confusion with pinene. Owing to the absence of chemical proofs such a mistake could not be detected. Parry further makes objection to the method of citral determination used by Chace. In conclusion, Parry is of opinion that in establishing the pinene test the U. S. Department of Agriculture is committing a serious mistake, and that in many seasons it will be impossible to get pure lemon oils admitted into the U. S. A. unless the American Authorities bow to established facts and agree to recognise as normal the existence of traces of pinene even in the conditions laid down by Chace.

¹) Chemist and Druggist **75** (1909), 786.

²) Chemist and Druggist **75** (1909), 875; Americ. Perfumer **4** (1910), 214.

The assertions of Parry are denied by H. W. Wiley¹⁾, Chief Bureau of Chemistry of the U. S. Department of Agriculture. This author declares that the American Authorities were quite aware that the requirements of the U. S. Pharmacopoeia, so far as concerns the rotation of the first 10%, could not be maintained, but he asserts that the objections raised in the year 1907 were founded upon the exceptionally high pinene content of the oils in question. Thorough investigations had shown that no pinene was to be detected in pure oil if, in the process of distillation, the rules laid down by Schimmel & Co. were carefully observed. One undoubted result of the requirements set up by the Bureau is that since the introduction of the test no single parcel of oil has been imported to which it has been found necessary to raise objections. Wiley further states that the Bureau of Chemistry has also worked out methods for the detection of added lemon oil terpenes, and expresses the highest expectations of the results of these methods.

H. E. Burgess²⁾ also adds a word on the subject. He holds that the best and easiest means of detecting the addition of turpentine consists in careful fractionation under diminished pressure and in the optical examination of the oil and of the first 10% of the distillate. As regards the detection of the terpenes of lemon oil, he refers to the investigations carried out by him several years ago in conjunction with Child.

As regards our own attitude towards the requirements set up by the Bureau of Chemistry, we maintain the position which we took up in our Report of November 1908 (p. 64); that is to say that when *traces* of pinene are found to be present great caution is demanded in judging the oil concerned. Even when the examination is conducted exactly according to the process described by Chace, the detection of very minute proportions of pinene is not, in our view, sufficient reason for rejecting a lemon oil as being adulterated.

Orange Oil. The Imperial Institute in London has forwarded to us a few samples of oils obtained by distillation in the West Indies. The constants of the samples were as follows: —

Oil from	d_{15}°	α_D	Solubility in alcohol of 90%
1. ripe oranges	0,8482	+ 91° 24'	in 5 to 6 Vol. a. o.
2. unripe oranges	0,8481	+ 94° 30'	" 4 " 5 " " "
3. unripe oranges	0,8490	+ 90° 22'	" about 5 " " "
4. entire oranges	0,8481	+ 97° 30'	" 5 to 6 " " "
5. orange peel	0,8500	+ 89° 4'	" about 5 " " "

¹⁾ Chemist and Druggist 75 (1909), 913; Americ. Perfumer 4 (1910), 220.

²⁾ Chemist and Druggist 75 (1909), 946.

Commercially these oils cannot be compared with the Sicilian oils obtained by pressure, since, owing to their having been prepared by distillation, they have suffered very considerable loss of aroma as well as of keeping-properties. We therefore refer to them merely as a matter of curiosity.

Eucalyptus Oil. Since pure eucalyptol has been available in any required quantity, the demand for all varieties of eucalyptus oil has decreased considerably. We continue, however, to have at our disposal a rich assortment of the current qualities, and we take this occasion to refer especially to our exquisite *Globulus* oil, which has a eucalyptol-content of over 80% and is well worth its price.

The distillate which is designated in our lists as "Australian eucalyptus oil" enjoys an increasing demand in the soap-industry and is being more and more used for cheap household-soaps on account of the small quantity required for scenting.

An official regulation has been published in the State of New South Wales, stating that eucalyptus oil for internal use must answer the following description¹): a colourless or pale yellow liquid, soluble in 3 parts of 70 per cent. alcohol, $d_{15.5}^2$ 0.910 to 0.930, $n_{D15.5}^2$ below 1.4800; eucalyptol content (to be estimated by the admittedly very untrustworthy phosphoric acid method), at least 50%. Mixed with one-third part by volume of phosphoric acid, the oil must congeal into a semi-solid mass. The bottles must bear the inscription "for human consumption". This order came into force on January 1st 1910.

Fennel Oil. Any manufacturer who, last autumn, may have made arrangements to work up the usual considerable quantities of fennel during the winter has probably been bitterly disappointed, for in those districts of Galicia where the bulk of the fennel is produced the result of last year's harvest was practically *nil*, and any parcels which came to market were held at prices which made it impossible to use them for manufacturing. It was fortunate that considerable stocks of oil had been left over from the season 1908/09, but these also have become greatly reduced in the meantime, although, of course, the high prices asked for them have precluded the use of fennel oil for several purposes. If it is taken into account that pure anethol is not much more than 50% dearer than fennel oil, it is clear that the use of anethol is more economical in a great many cases. Fennel of first quality, which in 1908 was quoted at about 30.— marks per 100 kilos, costs this season up to 55.— marks per 100 kilos.

¹) Pharmaceutical Journal 84 (1910), 48.

From a paper entitled "Contributions to the knowledge of fennel" by C. Hartwich and A. Jama¹⁾, we cull the following interesting morphological data. The length of the fruit of fennel ranges from 5,06 to 10,37 mm., although sizes exceeding 1 cm. are exceptional. The following table gives the comparative measurements of various varieties of fennel

Variety	Length mm.	Width mm.	Thickness mm.
Common	10,37	3,25	2,56
"	10,61	2,99	2,53
"	9,50	2,93	2,37
"	8,38	2,32	2,02
Roman (sweet)	9,91	2,65	2,68
Persian	7,39	1,95	2,52
Cretan or Levantine	7,09	2,48	2,70
Macedonian	6,30	2,12	2,54
Galician	5,11	2,08	2,14
East Prussian (Königsberg)	5,06	1,49	1,99

The authors submitted the abnormally large fruit (the varieties mentioned in the first two lines of the table), to closer examination when it was found that the deviations from type also existed in the anatomical structure of the fruit. The normal fruit has five primary ridges, but the varieties in question frequently possess several secondary ridges. They also had a larger number of secreting cells containing than the normal fruit, which has usually one vessel of this kind between each pair of ribs, and two between each channel.

It is said that the fruit of *Meum athamanticum* Jaqu.²⁾ is occasionally used as an adulterant for fennel, but it may easily be distinguished from the genuine seed by its brown colour, and by its taste, which reminds of fenugreek seed (*Trigonella Foeniculum graecum*). Anatomically also they are readily differentiated from fennel, because, whereas the *Meum*-fruit has from three to five secreting-cells (vittæ), between each pair of ribs fennel has only one.

Geranium Oil. Very little has been heard lately concerning African geranium oil. It is said that in the month of December the fields in the most important districts, suffered severely from hail with the result that prices were materially advanced, but according to the available reports it is extremely doubtful whether transactions of any importance took place at the quotation of about 30 frs. which was then current. Although the exports of geranium oil in 1909, as compared with 1908, show a shortage of nearly 6000 kilos (as will be seen from the statistics given below), it must nevertheless be taken

¹⁾ Berichte d. deutsch. pharm. Ges. **19** (1909), 396.

²⁾ Comp. Fischer-Hartwich, *Handbuch der pharmaz. Praxis*, Vol. I, p. 116, Berlin, 1900.

into account that the low values of the previous year had induced those chiefly interested to provide themselves liberally and that therefore the decreased production of 1909 was balanced by a lessened demand. It is reported that in Algeria the distillers are generally discouraged, because there is no longer any profit in the cultivation, but for the present we are unable to judge what degree of truth attaches to this report. It appears to be a fact, however, that in some districts geranium is no longer grown, because cereals pay better.

The exports of African geranium oil in the last three years have been as follows: —

1907	38700 kilos
1908	46600 „
1909	41000 „

The position of Réunion geranium oil in the course of the last six months has been still more obscure and difficult to judge. Owing to reports of a severe drought the prices advanced in October from 19 frs. to about 24 frs. and, singularly enough, the Syndicate has succeeded in maintaining them at this level, although the shipments in the latter part of the year also were very considerable. In December no fewer than 5370 kilos were shipped, bringing the total shipments for 1909 up to 57581 kilos, against only 34360 kilos in the previous year. When it is remembered that the world's consumption is estimated at about 30000 kilos annually, every sensible onlooker will admit that there is no reason for "talking up" the article and that its future cannot be regarded as particularly promising, unless ways and means are found of restricting the production within reasonable limits.

Gingergrass Oil. The scarcity which prevails in this article and the rise in prices resulting therefrom have had as a result that users are trying to dispense with this oil as far as possible; the demand has therefore been rather restricted, and the market was thus kept within certain limits.

Hyacinth oil. Some time ago Dr. Spalteholz, of Haarlem (Holland), extracted a volatile oil from hyacinths which, as is well-known, are cultivated in that neighbourhood on a large scale.¹⁾ The flowers were placed in tin containers immediately after being gathered, and were there left in contact for a few minutes with benzene which had been purified by the freezing-out process. After pouring off the benzene, and again washing the hyacinths with the extracting agent (381 kilos flowers being treated in this manner with 200 litres benzene), the solution was evaporated at 30° under reduced pressure to 2 litres. The fatty parts and the

¹⁾ Enklaar, Chem. Weekblad 7 (1910), 1; According to reprint kindly sent to us.

wax were then precipitated with dilute alcohol, filtered, and further evaporated *in vacuo*. The oil which was left (60,5 g = 0,016%) had, in its concentrated state, a disagreeable, acrid odour, and only acquired the natural hyacinth aroma when very highly diluted. The odour of the early-flowering varieties of hyacinth is finer than that of the late-flowering kinds, and the scent is pleasanter when the plants just begin to flower than afterwards.

Upon shaking with potash solution, Spalteholz was able to detect hydrogen sulphide in the alkaline liquid. He placed 10 g. of the oil at Enklaar's disposal for chemical analysis and of this quantity the latter used up to 7,7 g. First of all he freed the crude product from fatty oil and resin by freezing out the petroleum ether solution at -20° , obtaining by this means 3,6 g. of pure oil, which was split up into three fractions by distillation under 10 mm. press.: — I. b. p. up to 90° , 0,6 g.; II. b. p. 92 to 94° , 1,3 g; III. b. p. 94 to 150° , 1,7 g.

The first fraction contained a highly volatile body of a disagreeable odour, which was not further examined. In the second, Enklaar found a hitherto unknown compound, consisting of carbon, hydrogen and oxygen and possessing the following constants: b. p. 205 to 206° (760 mm.), 92 to 94° (10 mm.), $d_{15^{\circ}}$ 0,907, $\alpha_D + 1^{\circ}52'$, $n_{D16^{\circ}}$ 1,4914. Fraction III contained benzyl benzoate, and perhaps also free benzyl alcohol as well as esterified cinnamic alcohol; singularly enough, the benzoic acid which was liberated from the alkaline liquor had a well-defined odour of vanillin. There was further present in this fraction a fluorescent basic body, free from nitrogen, and of a narcotic odour. With acids this body turned red, with alkalis, yellow. Its properties reminded of oxonium-compounds. Neither methylester of anthranilic acid nor methylester of methylanthranilic acid could be detected, for when warmed with trinitrobenzene, which, with these bodies, yields a sparingly-soluble additive product, nothing but a reddish coloration ensued.

Hyacinth wax crystallises from alcohol in colourless flakes, which have the property of persistently retaining the odour of the flowers.

Juniper Oils. In spite of the unsatisfactory crops of juniper-berries last year, the prices of juniper oil have undergone no change. This is to be ascribed to the fact that large quantities of oil were still available from previous years, which it will probably take some time to clear off. In any case there is no prospect of a fall in the quotations within the near future.

Lavender Oil. It will be remembered that the lavender-crop of last year turned out unfavourably, with the result that in the course of the autumn the prices in the producing districts advanced to about

26 francs per kilo for 30% and about 29 francs for 40% oil. With slight fluctuations the market has remained at this level and it was not until a few weeks ago that a certain feeling of dulness set in. In any case the article will not fall in value before the next crop, as no very considerable stocks are left. If, however, the demand should become brisker, a further advance in the quotations may be expected with confidence.

According to a statement by J. H. Burkill¹), the drug which is known in Hindi as *Astukhudus* (*Ustukhudus*) is nowadays no longer obtained from *Lavandula Stoechas*, but from *Lavandula dentata*. The herb is used in the East both as a medicinal agent and in perfumery and is known to have been mentioned as long ago as the tenth century of our era under the name of *Astikus* or *Astodus*. In *Makhzan-el-Adwiya*, a book by an Eastern physician, the drug is referred to as *Astukhudus*. So long as the exchange of commodities between Europe and India followed the overland route, only *Lavandula Stoechas* was exported, but since trade has been exclusively conducted by sea, nothing but *Lavandula dentata* has been sent to India. At times other plants, such as *Prunella vulgaris*, have also been sold as *Astukhudus*.

Lemongrass Oil. The prices of this oil, which is an indispensable material in the preparation of synthetic violet scents, have remained at the previous level, and the market shows little animation.

The shipments from Cochin in the year 1909 amounted to 4448½ cases, distributed as follows: —

to London	709	cases
„ Liverpool	100	„
„ Havre	641	„
„ Marseilles	1519½	„
„ Hamburg	481	„
„ New York	998	„
Total		4448½ cases.

It is impossible to say what relation these shipments bear to the consumption, as the stocks which remain in the hands of consumers and on the European markets from 1908 and previous years cannot be estimated even approximately.

To the two lemongrass oils from Northern Bengal of which mention was made in our last Report²), we must now add three other samples

¹) Journ. and Proceed. Asiatic Soc. of Bengal (New Series) Vol. V, No. 2, 1909; from a reprint kindly sent to us.

²) Report October 1909, 75.

from the same source of supply, for which we are also indebted to the courtesy of Mr. I. H. Burkill, of Calcutta. All the oils are of special interest because they have all been distilled at various seasons from grass grown in one district, viz., Jalpaiguri. In July 1909, Mr. Burkill distilled grass before the flowering period, both locally (Ia) and in Calcutta (Ib). Two months later, in September, he again distilled before flowering (II). Finally he distilled a grass cut while in flower, first using the flowers only (III) and, for another experiment, the leaves only (IV). Hence, had the distillates differed in their characteristics, it would have been possible to draw definite conclusions as to the condition of lemongrass oil according to the stage of development of the raw material. No differences of any importance, however, were discoverable in the oil from the flowers and the leaves; these samples showed no material divergence from those prepared from herb before flowering, and no such differences were observable among the various oils distilled before flowering. The oil from leaves is a little richer in aldehydes and rather heavier than the oil from flowers, but the few investigations which have been made so far do not warrant any final conclusions. The constants of the various oils are enumerated in the table below: —

No.	Origin, condition, and time of collection of the grass	d_{15}°	α_D	Aldehydecontent	
				With NaHSO ₃	With Na ₂ S ₂ O ₃
	A. Non-flowering Jalpaiguri plants.				
I.	Cut in July. a) Distilled in Jalpaiguri	0,8954	— 0° 28'	90,0 %	84,0 %
	b) Distilled in Calcutta	0,8924	— 0° 49'	87,0 %	82,0 %
II.	Cut in September, distilled in Jalpaiguri	0,8925	— 0° 53'	85,5 %	83,0 %
	B. Flowering Jalpaiguri plants.				
III.	Flowers only	0,8897	— 1° 15'	83,0 %	79,0 %
IV.	Leaves only	0,8916	— 1° 5'	86,0 %	81,0 %

All the five samples gave clear solutions only at first, even with 90% alcohol; when diluted the solutions turned strongly opalescent.

An oil from Eastern Bengal, of which a sample was sent to us by the Imperial Institute in London, must also be included in the group of sparingly-soluble lemongrass oils. Its constants were as follows: — d_{15}° 0,9122, $\alpha_D \pm 0$, aldehyde content about 83% (sodium bisulphite). In the same class belongs a sample from New Guinea, with the following constants: — d_{15}° 0,8857; α_D — 0° 40'; aldehyde content 65% (sodium bisulphite). Both oils were sparingly soluble, a characteristic which they share with the West Indian oils.

With regard to the determination of the citral content of lemongrass oil, Parry¹⁾ expresses views which agree with those published by us some time²⁾ ago. The bisulphite- and the sulphite-tests gave different results, and in order to obviate misunderstandings it is therefore necessary always to state the method according to which the aldehyde-content of the oil has been determined.

We mentioned briefly in our last Report that the tsetse fly has been found to show a great aversion from citronella grass, and that therefore the cultivation of this plant might provide a protection against sleeping-sickness. Alluaud, in the *Journal d'Agriculture tropicale*, now states³⁾ that lemongrass has the same effect.

Limette Oil. A sample of lime oil sent to us by the Imperial Institute in London, which had been obtained by distillation in the West Indies, was found to possess the following constants: $d_{15^{\circ}}$ 0,8707, n_D^{20} $+35^{\circ}8'$, acid no. 1,5, ester no. 5,8, soluble in half its vol. of 90 per cent. alcohol; passing cloudiness when more alcohol (up to 2 vols.) was added, after which the sample became clear again. The oil is similar to the "distilled oil of limes" which is chiefly used in America, and of which the value is far below that of the product obtained by pressure.

Linaloe Oil. No noticeable change can be recorded in this important article since last autumn, the firm feeling having been maintained. At times there was great delay in the arrival of supplies, and this was the cause that the prices were immediately, although only temporarily, driven up by a few marks. This state of things was occasionally taken advantage of by a few shippers for placing upon the European, and also, we are informed, upon the American market, qualities to which considerable exception could be taken. These parcels consisted of linaloe oil distilled from seed, which we have already described on a previous occasion and which cannot be regarded as a normal quality, either in respect to its constituents or its odour. Such parcels have been rejected not only in Hamburg and in Marseilles, but also in New York, and we earnestly caution perfumers against buying these oils; they will no doubt be offered in certain quarters as "genuine linaloe oils", which in fact they appear to be. It will be desirable in future, when asking for quotations, always to specify oil from linaloe *wood*, if it is desired to avoid disappointments which may possibly be costly. We shall be pleased at any time and without charge to examine in our laboratories samples of unusually "cheap" oils. Cayenne linaloe oil was offered in considerable quantities and

¹⁾ Perfumery and Essential Oil Record 1 (1910), 9.

²⁾ Report November 1908, 83.

³⁾ Journ. d'Agriculture tropicale 10 (1910), 63.

several important transactions have been concluded. Its exquisite quality gains more and more admirers and anyone who values a particularly rich oil with a beautiful *bouquet* should not be deterred from using it on account of its slightly greater cost.

A few years ago Theulier maintained¹⁾ that Cayenne linaloe oil differs from the Mexican oil in the absence from the former of methyl heptenone, terpineol and geraniol. Recently Roure-Bertrand Fils²⁾ have examined an oil distilled by themselves. They found it to contain 90,5 % l-linalool, 5,3 % d-terpineol and 2,4 % geraniol, which agrees with our own observations³⁾. They also declare that the oil probably contains 1,2 % nerol, but unfortunately it is not stated how this body was identified. We ourselves made no tests for nerol at the time. Furthermore, traces of methyl heptenone were discovered by Roure-Bertrand Fils.

Matico Oil. The *Archiv der Pharmazie*⁴⁾ has now published a paper on the results of Thoms' ⁵⁾ examination of matico leaves and matico oil of which the author had already given some particulars at the VII International Congress of Applied Chemistry in London, and we are thus able to complete our previous notes on the subject.

A sample of oil which we supplied to Thoms in the year 1907 and which had been distilled by us from Peruvian matico leaves, was found to possess the following properties: d_{20}^0 0,948, n_D^{20} — $16^\circ 40'$. It was free from ketones and contained 0,1 % phenols and 0,7 % acids (chiefly palmitic acid). Possibly the oil may contain limonene and dillapiol, but this could not be proved beyond doubt. A fraction boiling between 136 and 140° (14 mm.) contains a sesquiterpene closely related to cadinene and to caryophyllene. Judging by the molecular refraction, this body belongs to the group of bicyclic sesquiterpenes. Its properties are as follow: b. p. 138 to 139° (17 mm.) d 0,914, $n_D^{21} 1,512537$, $n_{C21} 1,50808$ (red H-line), mol. refr. 66,52 for the red H-line.

Another oil, distilled from leaves which had been obtained by Thoms from a Hamburg firm (the oil-yield being 0,4 %), had altogether different properties: d 0,9185, n_D — $4^\circ 55'$. This oil contained 0,8 % phenols, 4 % acids, (principally palmitic acid), and small proportions of aldehydes, and dillapiol. The examination of the leaves from which the two samples had been distilled showed not only that the leaves distilled by us and those procured from Hamburg were

¹⁾ Rev. gén. de Chim. **3** (1900), 262; Report April **1901**, 40,

²⁾ Roure-Bertrand Fils' Bericht, October **1909**, 45.

³⁾ Report April **1909**, 68.

⁴⁾ Arch. der Pharm. **247** (1909), 542.

⁵⁾ Apotheker Ztg. **24** (1909), 411; Report October **1909**, 78.

entirely different; but also that not all the leaves in each sample were uniform. Thereupon, in order to clear up the matico-question once for all, Thoms resolved to distil an oil from leaves of which the botanical origin had been ascertained beyond doubt. The above facts had already been mentioned in our previous Report¹⁾, but the following additional data are here given to complete the account.

The oil of *Piper camphoriferum* also contains a sesquiterpene alcohol with the following constants: $\alpha_D + 5^\circ$, $n_D 1,50208$. The oil obtained from *Piper lineatum* Ruiz. et Pavon consists for a large part of sesquiterpenes; the oil from *Piper angustifolium* Ruiz. et Pavon, var. *subverbascifolium* also contains a sesquiterpene in the parts which boil between 147 and 149° (12 mm.). The oil from *Piper acutifolium* var. *angustifolium*, with the base of the leaf rounded, contains a sesquiterpene alcohol with the following constants: b. p. 117 to 119° (11 mm.), $n_D 1,4714$; as well as a sesquiterpene which equals in weight about 55% of the essential oil, and which has the following constants: $d_{20^\circ} 0,916$, $\alpha_D - 10^\circ 50'$, $n_D 1,50542$.

Oil from the seed of *Monodora grandiflora*. In a previous Report we gave an account of the essential oil which had been distilled by Thoms²⁾ from the seed of *Monodora Myristica*. More recently R. Leimbach³⁾, has given particulars of a similar oil which he had obtained to the extent of about 30% from the seed of another variety of *Monodora*, viz. *M. grandiflora*, a plant which grows wild in Africa. This oil possessed the following constants: $d_{15^\circ} 0,8574$, $\alpha_{D15^\circ} - 46^\circ 15'$, acid no. 3,9, sap. no. 7 to 12. At room-temperature one part of the oil is soluble with $3\frac{1}{2}$ parts of 90 per cent. alcohol. The oil constitutes a mobile liquid of pale yellow colour with an odour of cymene. The taste is at first aromatic, afterwards bitter. The sample was split up into four sections: —

In the fractions with the lower boiling points, (b. p. 64 to 66° ; $\alpha_D - 50^\circ 16'$ to $-52^\circ 55'$), which consisted for the greater part of hydrocarbons of the formula $C_{10}H_{16}$, the author found 1-phellandrene, which he identified by the constants (b. p. 64 to 66° at 17 mm.; $d_{15^\circ} 0,8488$; $\alpha_D - 55^\circ 56'$; $n_{D17^\circ} 1,48014$) and by the nitrosite (m. p. 108 to 110°). While examining this phellandrene, Leimbach confirmed the observation which had already been made by Bacon⁴⁾ that the rotation of the hydrocarbon decreases when it is left standing. For instance, it was found that a fraction of phellandrene of which the index of rotation was originally $-58^\circ 36'$, after having been left standing for

¹⁾ loc. cit.

²⁾ Comp. Report April 1904, 62.

³⁾ Wallach Jubilee publication (Göttingen 1909, Vandenhoeck & Ruprecht) p. 502.

⁴⁾ Comp. Report October 1909, 56.

a month at a cool place in diffused daylight, had a rotation of -36° only. Leimbach also goes into the question of the determination of the m. p. of phellandrene nitrosite; observing that, as in the case with all bodies which are liable to decomposition, the melting point is reduced in proportion as the heating proceeds more slowly. Thus, at 99 to 100° the nitrosite melted after 3 to 5 minutes'; at 91 to 92° after 6 to 10 minutes' and at 80 to 82° after 20 to 25 minutes' heating.

It is highly probable that the fractions with the lower boiling points contain, in addition to phellandrene, small quantities of camphene. p-Cymene was found to be present in the portions boiling between 70 and 85° (20 mm.) and was identified by being oxidised into hydroxy-isopropylbenzoic acid. The fractions of the oil with the highest boiling points contain palmitic acid and most probably also a little carvacrol, but the major portion consists of a compound $C_{10}H_{16}O$, a pale yellow oil, b. p. 130 to 154° (30 mm.) ($d_{15} 0,9351$; $n_D - 9^\circ 14'$) to which the aromatic odour of the essential oil is in part due. In addition these fractions contain a sesquiterpene which has not been identified clearly so far (b. p. 260 to 270° ; $d_{15} 0,9138$; $n_D + 24^\circ$; $n_{D16} 1,50513$), and a solid body of unknown constitution, with a m. p. between 160 and 163° .

Oil of Mosla japonica. Y. Murayama¹⁾ has distilled this oil from the herb, the yield being 2% of the material. The oil contained 50% carvacrol, as well as p-cymene. According to a previous examination²⁾ the oil is said to contain 44% thymol.

Mustard Oil. The price of our own distillate has undergone no change during the period under review, but recently a firmer tendency has been reported, so that in any case no reduction in the quotations of mustard oil should be counted upon for some time to come.

Myrtle Oil. To the series of oils of myrtle of special origin of which we published the constants in tabulated form a year ago³⁾, we are now able to add an oil produced in Cyprus. According to its constants ($d_{15} 0,9174$; $n_D + 8^\circ 11'$; $n_{D20} 1,46357$; acid no. 0,3; ester no. 20,9; ester no. after acetyl. 63,9; sol. in its own vol. and more of 80% alcohol), it has most affinity with the oils from Asia Minor. Up to the present all attempts to introduce such oils commercially alongside of the oils from Spain and the South of France have been unsuccessful.

¹⁾ Journ. of the Pharm. Soc. of Japan **1909**, November. Through Pharm. Zentralh. **51** (1910), 35.

²⁾ Gildemeister and Hoffmann, *The Volatile Oils*, p. 660.

³⁾ Report April **1909**, 71.

Neroli Oil. Judging by the present state of the trees in Southern France, it is believed that the crop will again give rather less than a medium yield. A large proportion of the trees blossomed for the second time last autumn, and no crop is therefore to be expected from them this spring; other trees have severely suffered from the November frosts and are also out of the calculation as regards flowering. Hence the probable outturn of the crop to be gathered in May is estimated at about 1600000 kilos, that is to say, about the same as that of 1909. So far nothing definite has transpired with regard to the prices which the *Société coopérative des producteurs* is likely to pay this season, but it is to be expected that more regard will be paid than formerly to the wishes and the interests of the neroli oil distillers, for, as may be remembered, the quotations of 1.35 to 1.50 francs per kilo, which were made for flowers in 1909, caused general resentment. A price of from 0.75 to 0.90 francs per kilo is regarded as fair, and if this can be established, it will be possible to make a proportionate, that is to say a not inconsiderable, reduction in the prices of neroli oil as compared with those of last year. The autumn-flowering of 1909 has yielded a crop of 270000 kilos, from which about 200 kilos of oil have been produced. Owing to the high values of the past few years the neroli oil trade has not been particularly brisk, for there was a well-founded objection to the payment of fancy-prices for the article, especially in view of the fact that in our artificial neroli oil a substitute was available, the excellent qualities of which are universally admitted. For this reason the present stock of neroli oil in the South of France is still fairly large.

An oil from the flowers of the sweet orange, which was sent to us from the South of France, (Portugal oil; *Essence de Néroli Portugal*), had the following constants: d_{15° 0.8686, $n_D^{45^\circ}$ 1.47352, acid no. 1.8, ester no. 16.7; soluble in one half its vol. of 90% alcohol; after diluting to five vols. opalescence ensues. We only refer to these properties as a matter of curiosity, as these oils are of no commercial importance whatever.

According to a preliminary communication by M. A. Chapus¹⁾ on Algerian oils of neroli and petitgrain, several varieties of orange oil are distilled in Algeria, especially in the neighbourhood of Blida, but the preparation takes place in a very primitive manner, and without any selecting of the distilling-material. For the purpose of comparing the Algerian oils with the French oils of commerce, Chapus caused the flowers of certain particular species to be gathered, and

¹⁾ Journ. de Pharm. et Chim. VI. 30 (1909), 484.

from them he distilled oils which were found to possess the following constants: —

	d_{15}°	α_D	Ester content ($C_{10}H_{17}OCOCH_3$)
1. Neroli oil	0,8723 to 0,8768	+ 5° 42' to + 6° 6'	25,26 to 31,99%
2. Portugal oil	0,8731	+ 26° 15'	34,18%
3. Petitgrain oil			
a) bitter	0,8755	— 5° 5'	42,49%
b) sweet	0,8705	+ 21° 33'	21,62%

From the above it appears that Algerian oils of neroli and portugal are much richer in esters than are the French and Spanish distillates. In our opinion this is probably due to the less careful selection of the distilling material, and does not necessarily give any superiority to the Algerian oils, which, in fact, may possess to some extent the characteristics of petitgrain oil. Unfortunately the author does not say whether the Algerian oils also equal the French and Spanish oils in respect of odour. Moreover, as was to be expected, Chapus obtained oils of different characteristics from the same native species according to the place where the flowers were grown, thereby once more confirming the old experience that, in addition to the manner of distilling, the climate and the variety of the material may be of the greatest influence in determining the quality of an oil.

Nutmeg Oil. There has been no lack of suitable material for distilling, and in consequence we have been able to replenish our supplies on most favourable terms.

In the course of manufacturing a dipentene-preparation from nutmeg oil, we were led to renew the investigation of some of the other constituents of the oil, and in particular of its hydrocarbon and alcohol fractions. F. B. Power and A. H. Salway¹⁾, by their excellent researches which were discussed at length in our Report at the time, had already shed considerable light upon the various constituents of the oil.

The oil-sample which we examined was of our own distilling, and had the following constants: d_{15}° 0,9109, α_D + 20° 5', n_{D20}° 1,4792. It contained about 70% of terpenes and from 7 to 10% of alcohols. The fractions with high boiling points constituted about 22% of the whole. Two kilos oil yielded 1375 g. hydrocarbons. Of this quantity 600 g. boiled between 156 and 159° (α_D + 32° 40'; d_{15}° 0,854) and were found to contain pinene and camphene; 775 g. boiled between 159 and 180°. The fractions boiling between 162 and 166° (d_{15}° 0,850, α_D + 42° 30') also consisted mainly of camphene. We were able to prove the presence not only of the well-known α -pinene but also of β -pinene by oxidation into nopinic acid. This acid, of which only

¹⁾ Journ. chem. Soc. 91 (1907), 2037; Report April 1908, 74.

A small quantity was obtained from 200 g. of the hydrocarbon fraction, had a m. p. of 126 to 128° (from benzene) and possessed only very little rotatory activity.

The fraction which boils between 170 and 180° consists, according to Power and Salway, of dipentene, but we were unable to obtain this body from it in a reasonably pure state. It is true that we succeeded in identifying the hydrocarbon which had already been found by Semmler, by means of the tetrabromide melting at 122 to 124°, but the fractions of which the b. p. lies between 170 and 180° appear to consist of a mixture of various terpenes. The optical activity of the fraction (which has also been observed by Power and Salway) indicates the presence of an active terpene. We further succeeded in establishing the presence of p-cymene (p-hydroxyisopropylbenzoic acid, m. p. 155 to 156°).

The alcohol fraction (b. p. 68 to 110° [5 to 5,5 mm.]) contains, according to early statements by Gladstone and Wright¹⁾ an alcohol called myristicol; but Power and Salway have shown that this body consists in fact of a mixture of various alcohols, among which are terpineol, linalool, geraniol, borneol, and an unknown alcohol.

The larger proportion of the alcohols in the oil-sample examined by us boiled between 205 and 225° and agreed, as regards its properties, with the alcohol-mixture of Power and Salway. The first runnings contained linalool and the fraction which passed over last, geraniol. The principal portion was reducible by fractionation into parts of higher and lower b. p. The mixture of alcohols boiling between 215 and 220° (d_{15° 0,9302; $\alpha_D + 9^\circ 21'$) consisted of α -terpineol, which had already been found by the two English chemists. In spite of strong cooling and inoculation this fraction did not solidify; nor did we succeed in obtaining a phenylurethane. On the other hand, we obtained with nitrosyl chloride a nitrosochloride, of which the nitrol-piperidin had a m. p. of from 156 to 158°.

The fraction which boiled between 205 and 215°, constituting nearly two-thirds of the whole mixture of alcohols, was split up into several portions which agreed with each other in the matter of physical constants. The main portion boiled between 209 and 212°; constants: d_{15° 0,9352, $\alpha_D + 14^\circ 51'$, n_{D20° 1,47853. When cooled down it remained liquid. Neither a phenylurethane nor a nitrosochloride was obtained. When heated with concentrated formic acid terpinene was formed, and when hydrochloric acid was passed into the solution of glacial acetic acid the result was a terpinene dihydrochloride, m. p. 50 to 52°. Oxidation with the calculated quantity of

¹⁾ Comp. Gildemeister and Hoffmann, *The Volatile Oils*, p. 367, for the composition of the oil.

permanganate in 0,5 per cent. solution produced a liberal yield of dextrorotatory glycerol, which melted between 112 and 115° when re-crystallised from chloroform. The other bodies formed during the oxidation-process were not isolated. 30 g. alcohol of the fraction boiling between 209 to 212° yielded 15 g. of pure glycerol, which seems to indicate that the alcohol from which the glycerol derives by oxidation occurs in this fraction in a high degree of purity. When the glycerol was boiled with dilute hydrochloric acid, water was split off, a mixture of p-cymene and carvenone being formed. The semicarbazone of the ketone melted at 200° . With carvenone semicarbazone its m. p. was not depressed. The alcohol which occurs in the fraction boiling between 205 and 215° is consequently identical with the terpinenol-4 which has been more closely investigated by Wallach¹⁾, and the alcohol described by Wright as myristicol (b. p. 212 or 212 to 218°) is therefore merely terpinenol-4 contaminated with α -terpineol.

From the fractions boiling between 205 and 225° , in which Power and Salway detected the presence (in addition to linalool, terpinenol and geraniol), of borneol, by oxidising that body to camphor, these same investigators in the course of the process of oxidation with chromic acid mixture, obtained a diketone $C_8H_{14}O_2$, of which the dioxime melted at 140° . As these fractions contained no appreciable quantities of compounds other than alcohols, Power and Salway concluded that in the process of oxidation their diketone had been formed from an unknown alcohol. But this unknown alcohol of Power and Salway, which these two investigators, by reason of the diketone-yield, did not regard as forming the principal constituent of the alcohol-fraction, is without doubt identical with terpinenol-4, while the diketone is identical with ω -dimethyl acetonyl acetone, obtained by Wallach²⁾ in the subsequent oxidation of the abovementioned glycerin from terpinenol-4, by way of the α, α' -dihydroxy- α -methyl- α' -isopropyl adipic acid, and of which the oxime melts at 137° . Our Report of November 1908, p. 180, contains a graphic representation of the formulæ showing this conversion, especially the generation of the diketone from the alcohol.

The result of our investigation, therefore, shows that besides α -pinene, camphene and dipentene, the hydrocarbon fractions contain β -pinene and p-cymene, and that the unknown chief constituent of the alcohol fraction is d-terpinenol-4.

Origanum Oil. According to the *Cyprus Journal*³⁾, last year's crop of origanum oil in the Island of Cyprus amounted to 1772 lbs.

¹⁾ *Terpene und Campher*, Leipzig 1909, p. 486; Report April 1907, 133 November 1908, 180.

²⁾ Liebigs Annalen **362** (1908), 264.

³⁾ Through Chemist and Druggist **75** (1909), 834.

The reduction as compared with the previous year is due to a fire which is said to have destroyed a large quantity of cut herb in store. But for this accident, it is said, the output of oil would have been larger than before. The oil which has been distilled is said to be of particularly good quality owing to the improved stills now in use.

Orris Oil. Our informants have sent us the following communication, dated middle of March, which we reproduce without comment: —

In our last report we already referred to an unexpectedly strong demand for Florentine orris root, which had developed at the time, and since then new orders have constantly come in at short intervals. It therefore appears as if in spite of substitutes and notwithstanding the increased prices, Florentine orris is able to maintain its old position in high-class perfumery. The previous estimate of the crop of 500 tons having been proved correct, the total stock of Florentine orris root was

at the beginning of September 1909 about 760 tons,
deduct shipments from 1st September 1909 to 28th February 1910 „ 370 „

remains at end of February 1910 about 390 tons.

Of the last-named quantity about 140 tons have been bought up within the last fortnight in order to cover orders, some of which were old while others had newly come in. Hence the total available quantity in Florence and district on March 12th 1910 reached the modest figure of about 250 tons. Add to this that the desire for buying continues both here and abroad, and it is not astonishing that the growers in the country districts are constantly increasing their prices and that some of them are already expecting to be able to sell sorts at the parity of 85 marks cif. Hamburg. About a fortnight ago we were still able to execute a few orders at the parity of 77/78 marks cif. Hamburg for sorts, but since then 79/80 marks has been repeatedly paid. Account must be taken of the small total stock amounting to

250 tons at end of February 1910, against	
750 „ „ „ „ „	1909 and
780 „ „ „ „ „	1908,

and of the prospect of a moderate crop, the latter, owing to the reduced plantations laid down last year, being estimated at a maximum of 500 tons. The conclusion seems therefore unavoidable that in the future the article will become dearer rather than cheaper. According to our spring report of 1909, the average annual exports of the preceding six seasons, ending August 1908, were 692 tons, and the average yield of the six crops from 1902 to 1908, 710 tons. On the other hand the exports in the year from September 1908 to August 1909 were 755 tons. In the six months closing at the end of February 1910 the exports were 370 tons. As stated above, only 250 tons are available for export in the next half-year from March to September 1910, as against previous half-yearly exports of: —

March/September 1909	490	} i. e. average 309 tons.
March/September 1908	265	
March/September 1907	140	
March/September 1906	370	
March/September 1905	280	

Naturally, the considerable enhancement of the prices mentioned in the above report has reacted upon the prices of orris oil, as the supplies of cheap orris root from previous seasons are now exhausted.

If the demand for our two qualities (of which the tenfold concentrated oil continues to be especially popular among the manufacturers of fine scents) continues in its present dimensions, we shall be compelled shortly to increase our quotations again.

H. Blin¹⁾, in *La Parfumerie moderne*, describes the cultivation of orris root, of which the Grasse factories consume about 300 000 kilos annually, most of which they obtain from Italy, chiefly from Florence. The author thinks that it would therefore be very desirable to extend the cultivation of orris in France, any surplus after satisfying the local requirements to be exported. As it is necessary to clean and dry the root before shipment the cultivation can only be made to pay where the soil is arid and labour cheap, as is the case on the French Mediterranean littoral. In Italy almost the only cultivated variety of the different kinds of orris is *Iris pallida* var. *Clio*. The cultivation of which is the same for all varieties of orris, offers no difficulties especially as the plants are not particular as to the richness of the soil. Manure is applied at the rate of about 6 tons per acre (15 000 kilos per hectare); so far, artificial manures have not yet been tried. The first crop is gathered after two or three years and a yield of from 2500 to 4500 kilos per hectare (10 to 18 tons per acre) can be expected.

Palmarosa Oil. Last autumn, the market showed rather a weakening tendency, but its subsequent development has caused a certain amount of surprise, for it soon became evident that the output was unequal to the requirements. Under the influence of a strong demand the quotations in India gradually advanced to 9/-, and even at this price, which still prevails, only insignificant quantities are offered. It will therefore be well to expect great scarcity of the article within the next few months, unless it should turn out that large quantities of palmarosa oil are held back by the native houses with speculative intentions. The new season's oil, as is well known, is not ready for shipment until October, so that several months have to be tided over. In any case, those consumers are to be congratulated who have filled their requirements for the year upon the basis of the quotation of 6/- which was in force in October.

In our last Report²⁾ we published an illustrated description of the distillation of palmarosa oil in the district of Amraoti, British India. Mr. I. H. Burkill, of Calcutta, to whom we were indebted for the in-

¹⁾ *La Parfumerie moderne* 3 (1910), 13.

²⁾ Report October 1909, 88.



Distillation of Palmarosa oil at Kandesh (British India).

ormation then presented, has in the meantime had the kindness to supply us with further details respecting the distillation of this oil as generally practised in British India. On this occasion also he has accompanied his description with several very successful photographs, a couple of which, being of particular interest, we incorporate in the present Report. We gladly seize this opportunity of expressing our sincere thanks to Mr. Burkill.

The illustrations show the distilling-plants in general use in the district of Kandesh, westward of Amraoti. As a rule, the stills there are covered-in with a roof, and closed with a large piece of wood. The *modus operandi* is the same as described in our last Report; but whereas in Amraoti a little common salt is thrown the stills every other day, this is very rarely done in Kandesh, where, moreover, the distilling period is much more protracted. Both palmarosa and gingergrass are distilled in Kandesh, the former in the low-lying districts, the latter on the plateau of Akrani. At the intervening altitudes the two oils are distilled alternately, the palmarosa grass available being taken first, and after that the gingergrass. The oil from the latter is sent to Bombay *via* Taloda and Nanderbar. Mr. Burkill has also sent us a collection of samples of oils distilled in Kandesh, and we present below the results of our examination of these¹⁾.

No.	Place of Production	d_{15}°	α_D	n_{D20}°	Acid No.	Ester No.	Total-Geraniol	Solubility in 70% alcohol
Palmarosa oils (Motia oils)								
1.	Chitar	0,8904	+0° 6'	1,47 225	0,8	39,8	91,5%	1,5 vol.
2.	Kumbi	0,8911	+0° 5'	1,47 176	1,0	47,3	90,7%	1,5 "
3.	Mohana	0,8906	+0° 20'	1,47 264	0,8	34,8	92,0%	1,5 "
4.	Naoli	0,8903	+0° 15'	1,47 205	0,5	40,7	93,0%	1,5 "
5.	Ragarwal	0,8946	-1° 20'	1,47 382	0,8	38,4	88,2%	1,5 "
6.	Udhala	0,8906	+0° 35'	1,47 225	0,8	38,7	92,4%	1,5 "
Gingergrass oils (Sofia oils)								
7.	Astumber	0,9396	-19° 42'	1,48 996	6,2	10,2	39,2%	2,2 vol. if more cloudy
8.	Bandhara	0,9372	+15° 20'	1,48 967	2,0	10,0	42,6%	2,1 " " " opalesc.
9.	Chanseli	0,9392	+38° 47'	1,49 082	5,3	8,0	41,1%	2,2 " " " cloudy
10.	Rapapur	0,9533	-27° 15'	1,49 252	4,5	8,8	48,1%	1,8 " " " "

All the palmarosa oils were soluble in from 3,4 to 3,6 vols. and more of 60 per cent. alcohol. All the samples possessed the typical characteristics of their respective kinds; the odour of the palmarosa oils Nos. 5 and 6 is somewhat less good than that of the others.

Patchouli Oil. In the course of the past year there has been a noticeable alteration in the position of this important oil, inasmuch

¹⁾ For the palmarosa and gingergrass oils previously sent to us by Mr. Burkill see Report April 1907, 58; April 1909, 56.

as the arrivals of Indian oil from the Straits Settlements have ceased entirely. During the past few years these oils had flooded the market everywhere, and under stress of their competition the price had fallen to such an extent that the distillation of patchouli here in Europe had become scarcely profitable. It is now reported from the other side that for some considerable time the manufacture there has been attended with great loss, and that there is all the less inclination to continue an unprofitable branch of industry because it is now much more advantageous to cultivate Pará rubber than patchouli. One result of the suspension of the distillation has been that during the past few months patchouli herb has been offered much more plentifully and advantageously than before, and that the distillation of patchouli in Europe again promises to become profitable. It is rumoured, however, that the cultivation of patchouli in the East is gradually being abandoned for other more profitable cultivations.

Pennyroyal Oil. Business in this article during the past few months has been very quiet. During the scarcity of pennyroyal oil which has prevailed for several years, soapmakers, it appears, have accustomed themselves to use other oils in its stead. At any rate we know of no other valid grounds to account for the absence of large orders on the part of the soap-industry. American pennyroyal oil is also once more available in sufficient quantities, but owing to its high price (\$ 1.60 per lb.) it plays no part on the European market.

Peppermint Oil, American. As early as the month of October it became evident that in our last Report on the position of the article we had formed too optimistic a judgment and that the stocks of oil were in reality considerably smaller than had been estimated originally, besides which, owing to the extraordinary conditions of weather which prevailed during the summer of 1909, the oil output had reached only about two-thirds of a normal average crop. As a result prices became firmer in the course of the autumn, and the position of the article was further strengthened by the fact that in quite a short time about one-half of the new distillate was taken out of the market by middlemen, whose object was to draw the greatest possible advantage of the upward movement in prices which was definitely expected. There was a continuous strong demand, especially for the better qualities, with the result that in America the value shortly rose to about \$ 2 per lb. for new crude oil, and this price still prevails. A further rise is not at all impossible, because the owners of the few parcels of good oil which still remain in first hand are very firm, and are not compelled to sell. Thanks to the efforts of our New York branch we have been able to supply our requirements in good time, and it will therefore not be necessary for us to advance our own price

a sympathy with the general rise. This news will no doubt be received with pleasure by the many friends of our well-known brand "F. S. & Co." After the most recent reports received from the other side, it remains somewhat doubtful, however, whether we shall be able to avoid holding for an advance, for the unusually brisk development of general business in the United States, which has taken place since the beginning of the year, may shortly bring with it an increased demand for peppermint oil.

According to a report from our New York friends, dated at the beginning of February, it is still too soon to say anything concerning prospects for this year's crop, but it is already certain that the plants have stood the winter very well, having been protected throughout the season by a thick layer of snow. The roots look better than they have done for years, and it appears, moreover, that a new method has been discovered to protect them successfully from the spring-frosts which frequently cause so much damage.

The exports of American peppermint oil in the months from July to November (the figures for December are unfortunately not yet available) were as follows: —

	1909	1908
July	9082 lbs.	7961 lbs.
August	4390 „	8269 „
September	8097 „	23022 „
October	19175 „	21393 „
November	21856 „	19675 „
Total	62600 lbs.	80320 lbs.

According to information obtained by our friends, the quantities which remained available in Michigan and Indiana at the end of February amounted to about 127000 lbs.

Peppermint Oil, English. Since the publication of our last Report, the prices of this article have remained entirely unchanged, business being very slack. In comparison with the excellent quality of our rectified American peppermint oil "F. S. & Co.", English oil is much too dear, and only a few manufacturers nowadays are able to afford the luxury of using Mitcham peppermint oil, in view of the general endeavour to cheapen manufactured articles as much as possible. We will not touch further upon the question of quality on this occasion, having so often exhaustively referred to this important subject that it will suffice if we again sound a warning against the qualities which are offered from all sides at less than cost-price. It is certainly very inadvisable to base purchases of Mitcham peppermint oil upon cheapness of price.

Peppermint Oil, Japanese. On page 99 of our last October Report we gave an estimate of the last crop. At the end of November our informants completed this by stating that the actual output for the district of

Bingo Bitchiu	was about	13 000 kin
and Hokkaido	„	120 000 „

the total result of the crop being therefore about 133 000 kin. Notwithstanding this fact, the tendency for menthol and for oil remained equally firm, for the stocks in Europe and the United States had been greatly reduced and there was every reason for expecting a demand proportionate to the general revival of business. The market therefore advanced in sympathy with these circumstances, and at the end of the year the quotations were about 9/- cif. for menthol and 5/10 cif. for oil. It is said that a fairly active business has taken place at the advancing prices, with the result that at the beginning of the present year the demand, especially for oil, fell off somewhat and the values became correspondingly easier. At the present moment the quotations are, menthol 8/3 and oil about 5/1, but a firmer tendency is again reported; for the near future, therefore, prices are likely to rule higher. It depends of course principally on the stocks which still remain in the East, and secondly on the financial necessities of the owners, what shape the market will assume in the future. As the general state of business promises to improve in Japan, there is probably little reason for expecting that the producers and middlemen will show themselves more tractable. It should be remembered that the menthol market in particular has often brought very unexpected surprises, and that in the United States menthol is described, not without justification, as the "football of the drug trade"¹⁾.

Peppermint Oil, Saxon. Very little remains of last year's production, the numerous buyers of this first-class quality having filled their requirements by contracts. Owing to the mild winter, the fields are in excellent condition, and unless severe frosts in the spring should cause damage, all signs point to a healthy development of the plants during the summer.

Parry²⁾ calls attention to an adulterant of peppermint oil which has not previously been observed. All the constants of a peppermint oil examined by him were normal, excepting the solubility, which left to be desired. By repeated fractional distillation Parry succeeded in separating 20 % of an oil with a rotation of -12° and a refractive

¹⁾ Oil Paint and Drug Reporter 1910, Nr. 8, II. 11.

²⁾ Chemist and Druggist 76 (1910), 293.

index of 1,43. The sample, however, was insufficient to determine the nature of the adulterant. Parry expects to be able to make further communications on the subject.

Petitgrain Oil. There has been no change worth mentioning in the market position of this article, and we regard the present quotations as reasonable. The shipments were regular and the demand has moved within normal limits. The quality of the supplies was not always above objection, but where claims ensued they appear to have been due less to adulterations than to the fact that the necessary care had not been taken in selecting the distilling material.

In a very interesting article in the Brazilian paper *Le Messager de São Paulo* of 9th July 1909, Dr. Dario Freire points out that it would be possible to prepare petitgrain oil advantageously in certain districts of Brazil. The author, however, starts from the erroneous assumption that in Paraguay petitgrain oil is worth from 30 to 35 francs per kilo, and we may therefore point out that there have been times when the article was not worth more than 10 francs per kilo. Before investing capital in the petitgrain industry in Brazil, it would be well to consider the possibility of working at a profit at so low a price as 10 francs, a matter which we think we are justified in regarding as doubtful. We believe it of interest to give our readers a few abstracts from the article referred to, at any rate in so far as regards the history of the petitgrain oil industry in Paraguay. It is stated that the credit for its establishment is primarily due to Balanza, a French botanist who came to Paraguay in 1873 and who took up the question of the industrial utilisation of the aromatic properties of the leaves of the wild orange tree which he had discovered in the course of his investigations into the *flora* of the country. In a book called *Le Paraguay*, published in 1892 in London and written by an English medical man, E. de Bourgade la Dardye, it is confirmed that Balanza established the first distillery of petitgrain oil. His method of manufacture, which was extremely primitive, is still generally followed in the country to this day. It is said that a distilling plant of this kind produces about 50 kilos of oil monthly. At present there are altogether 20 petitgrain oil distilleries in Jaguaron, 4 in Ita, 3 in San José de la Cordillera, 1 in Itacuruby, and 2 in Nemby, which between them have a capacity of from 2600 to 3000 kilos monthly, or about 36000 kilos annually. The article proceeds to state that, apart from the possibility of obtaining various essential oils from the bark, the flowers, and the leaves of the orange tree (not to speak of orange flower water), both the green and the ripe fruit can be used for preserves, while from the peel of the fruit a liqueur of the character of Curaçao may be prepared. The juice of the fruit is said to yield a refreshing beverage, which it is believed could compete with the native

rum (*caña*). Finally, it is said that the wood of the tree could be utilised in the manufacture of furniture.

The distilling plants are described as being very simple. Orange plantations are generally situated on a flowing stream, and a wooden shed covered with palm leaves and furnished with an oven heated with wood from the neighbouring forests forms part of the plant. The distilling apparatus consists of a boiler, in which the pressure does not exceed one atmosphere, and of a large container for the distilling material. The steam passes through a condensing worm which projects from the top of the still, and the distilled oil is collected in Florentine flasks. The daily output amounts to 3 to 4 litres oil, which is put up for shipment in specially made tins holding from 2 to 3 kilos, the tins being immediately closed by soldering.

Up to the present none of the efforts to improve the distilling plants have resulted in yielding a larger output (300 kilos leaves yield 1 kilo [= 0,33 %] of oil).

The establishment of a plant of this kind is very simple, and the labour not difficult. Each distilling operation takes 36 hours, and one man can do the stoking in at most 3 hours a day.

As already stated, we consider the views of Dr. Dario Freire, as far as Brazil is concerned, to be extremely optimistic.

A petitgrain oil of West Indian origin, distilled from leaves, was found to possess the following properties: d_{15° 0,8531, $\alpha_D + 43^\circ 36'$, acid no. 1,2, ester no. 6,1, soluble in 4 to 5 volumes of 90 per cent. alcohol, with slight cloudiness. These constants differ from those of the commercial oil, and besides, the odour also showed a difference, so that the oil appeared to be unsuitable for perfumery purposes. The sample had been courteously placed at our disposal by the Imperial Institute in London.

Some remarkable examples of adulteration of petitgrain oil have recently been observed by Parry¹⁾. He found two oils, which were suspected on account of their abnormally high sp. gr. (d_{15° 0,908 and 0,902 respectively), to contain an artificial ester, probably ethyl tartrate. Two other samples, with the following constants: d_{15° 0,904 and 0,9035, $\alpha_D + 2^\circ 30'$ and $+ 2^\circ$, ester content 43 and 46 %, showed unusually high acid numbers, which are ascribed by Parry to an addition of 15 % oleic acid, a surmise which was rendered still more probable by more careful examination. Attention is also drawn once more to the possibility of waste products in terpeneol-manufacture being used as adulterants; a possibility to which attention had already been drawn by J. C. Umney²⁾.

¹⁾ Chemist and Druggist 75 (1909), 410.

²⁾ Comp. Report October 1909, 156.

Pine Needle Oils. Fifteen years ago, on the occasion of a systematic examination of the so-called pine-needle oils¹⁾, we reported on an oil from *Pinus silvestris* L. which had been distilled by us from green pine needles collected in winter, the material having been specially gathered for us in December 1894. Since that time Tröger and Beutin²⁾ have taken up the examination of an oil from *Pinus silvestris* L., the material in this case, however, being distilled from young shoots collected in the spring. A large parcel of branches from *Pinus silvestris*, which we received some considerable time ago, afforded us an opportunity of once more, in our own works, distilling this oil, which is almost unknown in commerce³⁾ and at the same time of making experiments with a view of ascertaining in how far the mode of distillation affects the product obtained. The material was distilled partly dry and partly after having been soaked with water; the separate fractions as well as the oil from cohobation being each examined separately. Finally all the parts of the same oil were poured together and compared with a sample of an oil which had been obtained by one continuous process of distillation. The table below gives a review of the results obtained: —

	Oil %	d_{15}°	α_D	n_{D20}°	Acid no.	Ester no.	Ester no. after Acetyl.	Ester %	Total Bor-neol %
1. Dry Steam distillation									
a) Obtained after 3 hours	0,189	0,8721	+ 5° 36'	1,47 568	1,8	6,3		2,2	
b) " " another 4 hours	0,1	0,8797	+ 3° 45'	1,47 917	2,8	2,3		0,8	
c) from cohobation . . .	0,0075	0,8913	+ 1° 56'	1,48 306	4,1	10,9		3,8	
Total of a, b, and c . .	0,2965	0,8755	+ 5°	1,47 715	2,6	5,6	18,6	1,9	5,2
2. Water and Steam distillation									
a) Obtained after 3 hours	0,173	0,8773	+ 5° 31'	1,47 811	0,9	6,5		2,3	
b) " " another 4 hours	0,152	0,8882	+ 5° 50'	1,48 180	3,6	5,6		1,9	
c) a and b combined . .	0,325	0,8824	+ 5° 41'	1,47 996	2,4	6,0		2,1	
d) total distillate after 7 hours altogether . .	0,197	0,8822	+ 3° 10'	1,47 899	2,8	9,3	26,0	3,3	7,3

J. Swenholt⁴⁾ has recently described four different oils which he has obtained by distillation with steam under pressure from the branches and needles of conifers grown in the State of Colorado. As he had but a small quantity of material at his disposal he was only able to determine the constants of the oil.

¹⁾ Bertram and Walbaum, Arch. der Pharm. **251** (1895), 300.

²⁾ Arch. der Pharm. **242** (1904), 521; Report April 1905, 65.

³⁾ Comp. Report April 1909, 79.

⁴⁾ The Midland Drugg. and Pharm. Review **43** (1909), 611.

Oil from *Picea Engelmanni* (Engelmann spruce) had a well-defined odour of camphor. Its constants were as follow: $d_{20} 0,8950$, $n_D^{20} + 1^{\circ} 55' 38''$ (in a 5 cm. tube), sap. no. 24,15, corresponding to 8,5% bornyl acetate.

Oil from *Pinus murrayana* (Lodge pole pine) had a pleasant odour, not reminding of oil of turpentine. Sap. no. 51,87, corresponding to 18% bornyl acetate.

Oil from *Pinus edulis*. This oil also had an agreeable odour which was not like turpentine oil. Constants: $d_{20} 0,8653$, $n_D^{20} - 3^{\circ} 36' 58''$ (in a 5 cm. tube), sap. no. 17,55, corresponding to 6% bornyl acetate.

Most probably the water of cohobation of the oil from *Pinus edulis* contains formic acid. The author gives no information as to the oil yield obtained from his materials.

Oil of Rhus Cotinus. Perrier and Fouchet¹⁾ have distilled a colourless essential oil from the young twigs of *Rhus Cotinus* L., (syn. *Cotinus Coggygria* Scop., N. O. Anacardiaceæ) known in commerce as Zante fustic. The oil, which was obtained in a yield of 0,1%, had a faint odour of turpentine and possessed the following characteristics: — $d_{15} 0,875$, $n_D^{15} + 13^{\circ}$, $n_D^{20} 1,4603$, acid no. 6,1, sap. no. 34,3. It was soluble in 17 parts of 80 per cent., 10 parts of 85 per cent., and 3 parts of 90 per cent. alcohol, and was miscible in any proportion with 94 per cent. alcohol.

Rose Oil, Bulgarian. We need only refer briefly to this important article on the present occasion, for no events worthy of note have occurred in the Bulgarian rose oil market, although various attempts have been made to bring about some movement in the listless condition of the article in view of the impending increase in the duty on rose oil in the new French Customs tariff. But the ample production of the season 1909 and the large stocks which still exist, especially in the United States, are the factors which determine the movement of prices, and until the larger part of the available quantities has gone into consumers' hands, the position is hardly likely to change. So far no information as to the condition of the cultures at the close of the winter is available, and the publication of further statistical information must be deferred until our October Report.

In one of our last Reports²⁾ we pointed out the particular necessity of always testing rose oil for a possible addition of alcohol by determining the sp. gr. of the oil before and after extracting it with water, and observing whether there has been any increase after extraction. This mode of examination incidentally afforded us an opportunity of

¹⁾ Bull. Soc. chim. IV. 5 (1909), 1074.

²⁾ Report November 1908, 108.

observing, in the case of numerous samples from reliable sources, what was the influence exerted by the extraction with water upon the other physical constants of rose oil. As was to be foreseen, the rotation only suffers a slight change in the process, while on the other hand the refractive index always shows a noticeable increase, even with pure oils. We were able to ascertain that by the extraction with water the last-named constant rose up to 1,466 (25°). Henceforth therefore, this value must still be regarded as normal. As compared with the highest value of refraction previously mentioned by us (1,464 at 25°), this means an increase of 0,002.

In estimating the value of rose oil Umney¹⁾ urges that, in addition to the customary chemical tests, the odour-test should not be neglected. As the adulteration of the article is practised nowadays with incomparably greater dexterity than it was even ten years ago, it is not always easy to detect, by analysis alone, the presence of foreign bodies in the oil. It is, moreover, a striking fact that recently the geraniol content of rose oil has been greater than it was in former years. For instance, in 1896 the geraniol content of genuine oils varied from 69 to 73 ‰, whereas in recent seasons it has risen to 76 ‰, and even to 77 ‰. Umney, however, is in accord with our previous statements²⁾ that oils containing 75 ‰ of geraniol should be passed provided their odour is satisfactory. Parry³⁾ thoroughly endorses the views expressed by Umney. He is also of opinion that all preparations which mainly serve as adulterants of otto of rose are chiefly brought into commerce from Germany. A Bulgarian rose oil expert likewise backs up Umney⁴⁾ and expresses the wish that dealers and consumers should be enlightened, much more than has been done thus far, on the subject of the adulteration of rose oil. This expert's communications lead to the conclusion that the adulteration of otto of rose is practised in a very extensive manner in the country of origin itself, that is to say in Bulgaria. This conclusion has also been drawn by us in a previous Report⁵⁾ and shown in a graphical manner. It is said that the total production of oil in the year 1909 was only 130 000 oz. In the various warehouses this quantity grew to 175 000 oz., while the exports reached the figure of not less than 190 000 oz.

Rosemary Oil. The market in both varieties has been very slack indeed. Large parcels of Dalmatian oil of last season's di-

¹⁾ Chemist and Druggist 75 (1909), 786.

²⁾ Report November 1908, 108.

³⁾ Chemist and Druggist 75 (1909), 839.

⁴⁾ Ibidem 977.

⁵⁾ Report November 1908, 106.

stills still remain in the hands of the producers, while French oil suffers much from the keen competition of cheap Spanish oils, which greatly impede the sale of the French article. In Germany, owing to the revision of the denaturing-regulations for fat oils (see below), the demand for rosemary oil has fallen off very greatly.

Objections have been raised in several quarters to the increase of from 0,1 to 1,0%, in the proportion of rosemary oil which, in Germany, must be added to fixed oils for denaturing purposes¹⁾. In view of these protests the Prussian Ministry of Finance and the Saxon Department of Customs and Excise, with approval of the Imperial German Treasury Department, have again reduced the percentage till further orders to 0,2 (200 g. rosemary oil to 100 kilos gross of fixed oil), on condition that the rosemary oil which is used for the purpose shall first have been tested in regard to purity by an official chemist. The Government no longer lays down definite rules for testing the oil.

A Greek rosemary oil which was sampled to us behaved as follows: — d_{15}° 0,9148, $\alpha_D + 1^{\circ}37'$, α_D of the initial 10% of the distillate — $1^{\circ}30'$; soluble in its own volume and more of 80 per cent. alcohol.

Samphire Oil. To our previous communication on samphire oil²⁾ we are now able to add³⁾ that the fractions of the oil with low b. p. contain a terpene, b. p. 158 to 160°, d_4° 0,8703, $[\alpha]_D + 44^{\circ}37'$ (very probably d-pinene), as well as another terpene boiling between 176 and 180° (d_4° 0,8957, $\alpha_D \pm 0$) which has not been more closely identified.

Sandalwood Oil, East Indian. On the following pages we present, as customary, the results of the Indian auctions, from which it will be seen that about the same quantity of sandalwood oil was brought under the hammer last season as in 1908. The demand by European buyers at the auctions was exceedingly moderate, and the table of prices composed by us and given on page 95 shows sufficiently that the Government has again had every reason for complaining of lack of desire for buying. A portion of the most esteemed varieties could only be sold at considerable reductions in prices as compared with 1908, and the offers made by the large buyers were mostly so far below the views of the Conservator of Forests that important quantities of wood were again bought in (about 430 tons). In addition

¹⁾ Der Seifenfabrikant 30 (1910), 79.

²⁾ Report October 1909, 108.

³⁾ From a reprint kindly sent to us by the author since our previous communication

Comparative prices obtained in the sandelwood auctions of 1908 and 1909.

Auction	Tarikere		Chickmagalur		Hassan		Bangalore		Seringsapatam		Hunsur		Fraserpett		Tirthahalli		Sagar		Shimoga	
	7./12. 1908	29./11. 1909	3./12. 1908	2./12. 1909	30./11. 1908	6./12. 1909	25./11. 1908	9./12. 1909	23./11. 1908	13./12. 1909	19./11. 1908	16./12. 1909	16./11. 1908	18./12. 1909	17./12. 1908	22./12. 1909	14./12. 1908	24. u. 25./12. 1909	10./12. 1908	24. u. 25./12. 1909
Prices realised:—	cif d. w. p. cwt.	cif d. w. p. cwt.	cif d. w. p. cwt.	cif d. w. p. cwt.	cif d. w. p. cwt.	cif d. w. p. cwt.	cif d. w. p. cwt.	cif d. w. p. cwt.	cif d. w. p. cwt.	cif d. w. p. cwt.	cif d. w. p. cwt.	cif d. w. p. cwt.	cif d. w. p. cwt.	cif d. w. p. cwt.	cif d. w. p. cwt.	cif d. w. p. cwt.	cif d. w. p. cwt.	cif d. w. p. cwt.	cif d. w. p. cwt.	
2nd Class Billets . .	55/6	—	—	—	—	—	—	—	52/-	51/6	57/-	—	—	—	—	—	—	—	—	
3rd " . .	56/-	—	—	—	—	—	—	—	55/6	50/6	56/6	—	—	—	—	—	—	—	—	
Ghotla	—	—	—	—	—	—	—	—	55/3	50/6	56/6	—	—	—	—	—	—	—	—	
Ghatbadala	50/6	—	50/-	—	49/6	—	—	—	50/5	—	51/6	44/3 to 44/9	55/-	—	49/3	—	41/6 to 42/6	—	41/6 to 42/6	
Bagaradad	53/3	—	—	—	—	—	—	—	53/3	—	54/-	—	55/-	47/-	—	—	—	—	—	
1st Class Roots . . .	56/6	—	56/-	—	56/6	—	—	52/9	—	51/6	57/6	57/-	60/-	—	—	—	—	—	—	
2nd " . . .	56/6	—	55/-	50/-	55/-	—	52/3	—	—	49/9	57/6	56/6	60/6	—	—	—	—	—	—	
3rd " . . .	—	—	—	—	—	50/-	50/-	—	—	47/9	56/6	—	60/-	—	—	—	—	—	—	
1st " Jugpokal. .	47/-	—	47/-	44/3	47/6	46/-	—	—	—	—	—	42/9	54/-	—	44/6 to 45/-	41/6 to 41/10 ¹ / ₂	44/6 to 45/-	40/6 to 42/6	—	
2nd " . . .	—	—	44/-	—	—	—	—	—	—	—	—	—	50/9	45/6	—	—	—	—	—	
Ain Bagar	—	—	—	—	—	—	—	—	46/-	—	46/-	—	55/-	—	—	—	—	—	—	
Cheria	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	
Ain Chilta	33/-	—	32/9	—	32/6	—	26/3	—	—	—	33/3	—	—	—	—	—	—	24/-	—	
Hatri Chilta	—	33/9	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	
Milwa Chilta	19/9	—	19/9	—	20/6	—	—	—	19/9	—	20/6	—	—	—	19/-	17/-	19/-	16/3 to 16/6	16/3 to 16/6	
Basola Bukni	14/6	—	15/6	—	—	—	—	—	—	—	—	—	17/-	—	14/6	11/9	—	12/-	12/-	

Description	Parikere		Chickmagalur		Hassan		Bangalore		Seringsapatam		Hunsur		Fraserpett		Tirthahalli		Sagar		Shimoga		Total	
	November 29		December 2		December 6		December 9		December 13		Dechr. 16		December 18		Decemb. 22		December 24		December 25		Tons Cwts.	
	Tons	Cwts.	Tons	Cwts.	Tons	Cwts.	Tons	Cwts.	Tons	Cwts.	Tons	Cwts.	Tons	Cwts.	Tons	Cwts.	Tons	Cwts.	Tons	Cwts.		
1st Class Billets . .	—	—	—	—	—	$1\frac{1}{2}$	—	—	—	4	—	—	—	—	—	—	—	—	—	—	—	—
2nd " "	3	9	—	—	12	13	—	—	11	11	9	5	—	—	—	—	6	11	2	15 $\frac{1}{2}$	63	$4\frac{1}{2}$
3rd " "	2	10	—	—	2	10	—	—	16	—	8	—	—	—	2	12	11	8	37	15	71	$19\frac{1}{2}$
Ghola	1	6	—	—	2	12	—	—	4	18	4	10	15	—	14	6	2	8	4	7	19	10
Ghatbadala	15	15	42	—	25	11	—	$16\frac{3}{4}$	18	—	—	—	10	—	—	12	2	2	46	10	261	$103\frac{3}{4}$
Bagaradad	6	13	—	—	8	10	2	10	5	5	11	—	5	—	11	11	$10\frac{1}{4}$	11	11	15	65	$19\frac{1}{4}$
1st Class Roots . .	8	$5\frac{3}{4}$	18	—	13	—	5	$3\frac{3}{4}$	12	11	21	10	7	—	15	3	$15\frac{1}{5}$	$\frac{34}{25}$	15	15	170	$12\frac{1}{2}$
2nd " "	7	5	6	—	4	5	4	$18\frac{3}{4}$	12	3	26	10	8	15	7	4	$18\frac{7}{12}$	4	13	15	102	$1\frac{1}{4}$
3rd " "	6	10	—	—	3	5	3	15	6	15	11	10	11	5	7	1	2	$\frac{19}{8}$	8	15	86	16
1st " Jugpokal.	22	$7\frac{3}{4}$	$\frac{18}{66}$	—	24	11	10	3	$\frac{30}{36}$	10	121	—	23	—	35	5	20	11	$\frac{77}{63}$	5	548	$7\frac{3}{4}$
2nd " "	10	13	$\frac{18}{10}$	—	9	15	3	$4\frac{1}{2}$	14	15	28	—	13	15	18	2	8	15	23	—	167	$19\frac{1}{2}$
Ain Bagar	7	10	—	—	6	$5\frac{1}{2}$	3	$5\frac{17}{4}$	5	—	10	—	7	—	9	16	$11\frac{1}{2}$	11	7	10	71	$17\frac{1}{2}$
Cheria	1	$13\frac{1}{2}$	* 1	1	—	$17\frac{1}{2}$	—	$10\frac{1}{2}$	1	$3\frac{1}{4}$	2	10	1	—	6	17	$6\frac{1}{4}$	2	$17\frac{1}{2}$	21	$15\frac{3}{4}$	
Ain Chilla	$\frac{15}{17}$	18	—	—	6	10	13	$1\frac{1}{4}$	$\frac{20}{11}$	—	26	—	—	$\frac{1}{13}$	$\frac{21}{13}$	$\frac{15}{16}$	$\frac{13}{13}$	$\frac{29}{18}$	10	233	$6\frac{1}{4}$	
Hatri Chilla	—	5	—	—	11	12	—	—	—	$16\frac{1}{4}$	5	—	—	—	—	4	—	—	—	1	$19\frac{1}{2}$	
Coita Chilla	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	3	2	
Milwa Chilla	16	$7\frac{1}{4}$	32	—	20	5	9	$17\frac{1}{2}$	27	—	86	—	—	—	11	14	3	15	63	311	$183\frac{3}{4}$	
Basola Bukni	8	$13\frac{1}{4}$	—	—	15	$2\frac{1}{2}$	6	$12\frac{1}{4}$	15	15	14	—	18	—	12	17	13	25	10	123	$23\frac{3}{4}$	
Saw Dust	—	$1\frac{3}{4}$	—	—	—	$5\frac{1}{4}$	—	—	$9\frac{1}{2}$	1	—	—	15	—	7	—	5	—	—	12	3	$15\frac{1}{2}$
Total	152	3	231	1	169	$3\frac{1}{4}$	66	16	250	6	450	—	200	$1\frac{1}{4}$	153	16	$136\frac{1}{2}$	519	12	2329	17	

* Last season's wood.

to this about 135 tons, mostly of inferior quality, remain in stock from the auctions of 1908.

In the course of the winter months business in sandalwood oil developed extraordinary activity, and important transactions were put through, although at very moderate prices. As we have already previously stated, our capacity of production has been very materially increased by the enlargement of our distilling plant which has lately been effected. The trade in this important article is more and more concentrating itself at our Works, thus affording proof that only the most up-to-date and practical methods of manufacture are still profitable, and that it is only possible to conduct this business on a rational scale by utilising most carefully all advantages which present themselves in purchasing. It is no wonder, therefore, that a large number of medium sized and small firms, who previously distinguished themselves by underbidding all reasonable quotations, have now been compelled to abandon manufacturing. The qualities which are offered by others, especially in England, sometimes lead to claims, especially because the guarantee of santalol content is at times somewhat liberal, the warrantors relying upon the difficulties which most of the buyers experience in carrying out santalol determinations.

Umney's¹⁾ Pharmacopœia-suggestions in regard to sandalwood oil ($d_{15,5^\circ}$ 0,973 to 0,985; α_D — 16 to — 20°; sol. at 20° 1 vol. in 6 of 70 per cent. alcohol) have induced Stafford, Allen & Sons, Ltd.²⁾, to publish their laboratory records relating to their own distillates from Mysore wood, extending over a period of 2³/₄ years. The constants of 172 oils showed the following range of values: d_{15° 0,9733 to 0,9860, α_D — 13,32 to — 20,85°, solubility: 1 in from 4 to 14 parts of 70 per cent. alcohol. Oils which dissolved badly invariably displayed an abnormal optical behaviour.

Although oils which are sparingly soluble and have a low rotatory power occur occasionally, we should not recommend the Editors of a Pharmacopœia to take them into consideration, because by doing so the detection of adulterations would be rendered much more difficult. We regard the values proposed by Umney as suitable for the purpose.

Semmler³⁾ has discovered that when a methyl alcoholic solution of santalene⁴⁾ (the sesquiterpene which can be isolated from the first runnings of sandalwood oil), is saturated with hydrogen chloride, it

¹⁾ Comp. this Report, p. 137.

²⁾ Chemist and Druggist **76** (1910), 293.

³⁾ Berl. Berichte **43** (1910), 444.

⁴⁾ Comp. Report October 1907, 85.

yields principally santalene dihydrochloride, $C_{15}H_{24}$, 2 HCl, which can only be distilled without decomposition under greatly diminished pressure and of which the properties are as follows: — b. p. 140 to 142° ($0,55$ mm.) $d_{20} 1,076$, $n_D 1,4976$. Upon reducing with sodium and alcohol a mixture is formed which consists probably of hydrocarbons $C_{15}H_{24}$, $C_{15}H_{26}$ and $C_{15}H_{28}$. By treating with ozone, Semmler eliminated the probably unsaturated hydrocarbons $C_{15}H_{24}$ and $C_{15}H_{26}$, retaining the saturated compound $C_{15}H_{28}$: tetrahydrosantalene (b. p. 116 to 118 [9 mm.]; $d_{20} 0,864$, $\alpha_D + 7^{\circ}30'$, $n_D 1,4676$). Dilute solution of permanganate of potassium does not react with tetrahydrosantalene neither does ozone, which facts confirm the saturated character of the compound, thus showing, according to Semmler, that the tetrahydrosantalene molecule contains only two rings.

Sandalwood Oil, West Indian. This oil, which is also prepared in our Works on the largest possible scale, has been very scarce during the last six months owing to the fact that the delivery of the important quantities of wood for which we had contracted has been somewhat delayed because of the absence of opportunity of shipment. A large consignment is shortly expected, and we then hope to be able to cope with any demand which may present itself.

Sassafras Oil. Evans Sons Lescher & Webb Ltd.,¹⁾ in their recently-published Analytical Report, enumerate the properties of two sassafras oils distilled by themselves, which we reproduce here on account of the interest connected with them from the fact that genuine samples of this oil are comparatively rare. The oils were soluble in 1,5 vols. of 90 % alcohol, and had the following constants: $d_{15,5} 1,074$ and $1,080$, $\alpha_D + 3^{\circ}30'$ and $+ 2^{\circ}22'$, respectively²⁾.

Spearmint Oil. This article was procurable last autumn — that is to say shortly after the crop — at low prices, but in the meantime its value has not inconsiderably advanced. At the advantageous quotations a good demand set in, and the larger part of the available quantities passed into the hands of dealers, whose endeavour it is not only to maintain the prices, but to draw the greatest possible profit from the market position. A further increase in the value seems probable in the course of the next few months.

Spike Oil. The last crop has only yielded a moderate result notwithstanding which no material change in prices can be recorded. This is probably due in the first place to the fact that the market has again been flooded with cheap so-called Spanish lavender oils most of which, although leaving very much to be desired in point of

¹⁾ Analytical Notes 1909, January 1910, 49.

²⁾ Comp. Report April 1906, 61.

quality, yet obtained a footing with many soapmakers owing to their low price. It may be assumed, however, that in most cases the employment of such oils has been attended by disappointment.

Star Anise Oil. Chinese oil apparently continues to be plentiful, for the prices have remained at their present level with slight fluctuations, most of which were caused by variations in the exchange rate of silver. It therefore appears that more of the oil is being produced than was anticipated by us, for the fact that the price has been the lowest on record has led to important transactions. Tonquin star anise oil, which is especially esteemed, has also been offered at favourable rates, and on this occasion also the greater part of the output has passed into our hands.

Besides anethol, of which star anise oil contains about 90%, the presence in the oil of the following bodies has thus far been ascertained: α -pinene, l-phellandrene, hydroquinone ethyl ether, methyl chavicol, anisic aldehyde, anisic acid¹⁾, and anisic ketone²⁾. According to Oswald³⁾, the oil also contains safrol, while Tardy states that it contains terpineol, a laevorotatory sesquiterpene, and a body melting at 213°. Absolute proof of the presence of the two last-named bodies, however, has not been given, and with regard to these, therefore, corroboration is required; hence it was thought desirable to repeat the investigation as regards the terpenes, especially in view of the knowledge which has been gained in the chemistry of terpenes in the course of recent years.

The hydrocarbon fraction had the following constants: b. p. 63° (13,5 mm.), d_{15}° 0,8601, $a_D - 22^{\circ}31'$, n_{D20}° 1,47226. The constants of the portions obtained by fractionation *in vacuo* were in mutual agreement. In the first fraction the presence of traces of α -pinene was shown by the nitrosochloride and nitrobenzylamine, m. p. 122 to 124°. The major portion of the hydrocarbons distilled between 173 and 176°. The fractions melting from 173 to 174° (d_{15}° 0,8535; $a_D - 24^{\circ}10'$; n_{D20}° 1,47226) contain l- α and β -phellandrene. In 1893 we⁴⁾ succeeded, by means of the nitrite, m. p. 102°, in identifying l-phellandrene as the principal constituent of the terpene-fraction. We now obtained chiefly a dextrorotatory nitrite, melting between 108 and 110°. A second, also dextrorotatory, nitrite, m. p. 100 to 102°, separated out from the crystallisation liquor. It is well known that both α - and β -phellandrene yield two nitrites each, which may

¹⁾ Gildemeister and Hoffmann, *The Volatile Oils*, p. 357.

²⁾ Tardy, *Thèse pour l'obtention du diplôme de Docteur de l'Université de Paris* (1902), p. 22; Report October 1902, 79.

³⁾ Arch. der Pharm. 229 (1891), 95.

⁴⁾ Report April 1893, 63.

be readily differentiated from each other by their melting points and their rotatory power. The properties of the nitrites of phellandren from star anise oil made it probable, of course, that the oil contained both α - and β -phellandrene, but in order to obtain certainty on this point, we attempted, starting from the nitrites, and proceeding by way of nitrophellandrene, to obtain carvotanacetone, or dihydrocuminic aldehyde. The ketone or mixture of aldehydes which was obtained in the course of this process had an odour of carvone, but it was impossible to obtain a uniform substance from the mixture by the aid of the semicarbazones. The poor quantitative yield of nitrite (15 g. from 100 g. hydrocarbon) prevented us from ascertaining the presence of β -phellandrene by this method. Therefore we oxidised the fraction boiling between 173 and 174° with 0,5 % solution of permanganate with cooling, in portions of 60 g. each. The neutral bodies were isolated with chloroform from the evaporated liquors of oxidation. These bodies boiled between 120 and 130° (5 mm.) and showed no inclination to crystallise. From 30 g. of the neutral product we then obtained, by heating with dilute sulphuric acid, 5 g. of a substance with an odour of cuminic aldehyde and cymene. The semicarbazone of the tetrahydrocuminic aldehyde melted at 202 to 205° , and the cuminic acid which was formed by oxidation with chromic acid melted at 113 to 115° . This proves the presence in the oil of β -phellandrene, so that it is now clear that both phellandrenes are constituents of star anise oil.

The hydrocarbons which were not attacked by permanganate when the phellandrene fractions were oxidised, were found to have a rotatory power of only $\alpha_D - 9^{\circ}30'$. Their odour reminded of cymene. The fractions boiling between 175 and 176° proved to be especially suitable for isolating cymene. They were treated by the cold process with dilute permanganate solution as long as the colour of the permanganate persisted. The mixture which had not been affected still contained cineol, which was separated from the cymene by shaking with resorcinol solution. The hydrocarbon which was thus obtained had the following constants: b. p. 175° , $d_{15} 0,8558$, $\alpha_D - 0^{\circ}18'$, $n_{D20} 1,47274$. By oxidising according to Wallach's method it yielded hydroxyisopropyl benzoic acid, m. p. 156 to 157° , which, when boiled with dilute hydrochloric acid, was converted into p-propenyl benzoic acid, m. p. 159 to 160° , thus proving the presence of p-cymene. The fractions boiling between 175 and 176° were those from which most cineol was isolated. It was more closely identified from the iodol-compound (m. p. 111 to 111°).

According to Tardy, the fractions boiling between 216 and 218° (218 and 224°) contain terpineol. So far, however, this assumption has not been proved, for the mere boiling-point and odour of

fraction are insufficient data for concluding the presence of terpeneol. The fractions containing terpeneol, when freed as far as possible by fractionation from methyl chavicol and anethol were found to possess the following constants: —

I. B. p. 94 to 97° (10 mm.), 215 to 218°, d_{15}° 0,9465, $\alpha_D + 8^{\circ} 35'$.
 II. „ 97 to 102° (10 mm.), 218 to 220°, d_{15}° 0,9498, $\alpha_D + 8^{\circ} 31'$.
 Both fractions had the characteristic odour of terpeneol, slightly disguised by small quantities of anethol. By treatment with hydrochloric acid, a good yield was obtained of dipentene dihydrochloride, m. p. 47 to 48°, with nitrosyl chloride a small yield of nitrosochloride, m. p. 113°. With phenyl isocyanate we obtained a urethane, m. p. 110 to 111°, which, with terpinyl phenylurethane, (m. p. 111 to 112°) showed no depression of the melting point. By oxidising with dilute permanganate solution the terpeneol was converted into the corresponding glycerin, which, with chromic acid, gave the keto-lactone, m. p. 62 to 63°, of which the semicarbazone melted at 200°.

Oswald, at the time, demonstrated the probability of star anise oil containing safrol, but since his investigations were made this body has not again been detected in the oil. Upon oxidising the high-boiling fractions (b. p. 215 to 230°) with permanganate, we obtained, in addition to anisic acid, very minute proportions of a solid aldehyde, m. p. 34 to 36°; m. p. of the semicarbazone 224 to 225°. A mixture of this semicarbazone with the semicarbazone of piperonal, which also melts at 224 to 225°, produced no depression of melting-point. As, before oxidation, the fractions contained no piperonal, this body can only have originated from safrol during the oxidising process. Therefore, the presence in the oil of traces of safrol affords no proof of adulteration with Japanese star anise oil.

The result of the examination, therefore, is to show that star anise oil contains p-cymene, cineol, safrol and terpeneol in addition to its previously-known constituents. The phellandrene present was found to be a mixture of 1- α - and β -phellandrene.

Oil of Storax. Two storax oils, offered as “guaranteed pure”, but below the market price, have afforded us another proof of the necessity of using caution when confronted with “cheap” offers. Samples of the two oils showed the following constants: —

1. d_{15}° 1,0986, $\alpha_D - 1^{\circ} 55'$, acid no. 0,5, ester no. 239,9, n_{D20}° 1,56149; soluble in twice its vol. of 80 per cent. alcohol with slight opalescence.

2. d_{15}° 0,8781, $\alpha_D + 19^{\circ} 20'$, acid no. 0,1, ester no. 5,0, n_{D20}° 1,47763, gave a slightly cloudy solution with 5 to 6 times its vol. of 90 per cent. alcohol.

The first sample raised suspicion at once by its high sp. gr., and the truly enormous ester number pointed straightaway to adulteration.

A more detailed examination revealed that the oil was simply benzyl benzoate scented with styrene, for when subjected to distillation under 4 mm. press., we obtained between 35 and 40° about 5% first runnings possessing the characteristic odour of styrene, while about 90% of the total oil passed over almost uniformly at 156 to 157° and possessed all the constants of benzyl benzoate: — d_{15}° 1,1246; n_{D20}° 1,57000, sol. p. + 18,1°, ester no. 262,3.

The second sample differed from the first in its very low sp. gr. its refractive index also was too low, its optical rotation, on the other hand, much too high. The suspicion which was naturally aroused that in this case also the oil was adulterated, was confirmed by its behaviour on boiling. By subjecting the oil to distillation we obtained one fraction of 45% which passed over under 757 mm. a from 156 to 160°, and which consisted of pinene (d_{15}° 0,8668; α_D + 21°33'; n_{D20}° 1,47225; m. p. of the pinene nitrobenzylamine 121,5°). As this hydrocarbon has not been met with in storax oils up to the present, and in any case cannot possibly occur in them to any large extent, it is quite certain from the values given above that the oil was adulterated with oil of turpentine in an almost incredible degree.

Oil of Tagetes patula. Prof. J. Pohl, of Prague, sends us the following information regarding a sample of tagetes oil¹⁾ which was forwarded to him last year for purposes of physiological examination: "The experiments carried out by me showed that the oil exerts no specific action whatsoever. It has a paralysing effect upon the spinal marrow, is antiseptic, and yields a glycuronic acid; in short, it plays all the familiar pranks."

Tansy Oil. As we had foreseen, the American output of the past year exceeds the requirements, and it is therefore not surprising that it has been possible further to reduce the prices by some marks per kilo.

Turpentine Oil. According to the *Oriental Druggist*, Yokohama, 3 (1909), Nos. 20 and 21, p. 2, the exploitation of oil of turpentine by the State has been projected for the Japanese part of the island of Sakhalien and the management of the undertaking is to be entrusted to a Military Pharmacist, Mr. Takata. In addition to other difficulties the authorities have to contend with frequent and devastating forest conflagrations caused by the camp-fires which the natives light to protect themselves from the cold.

A British Consular Report²⁾ mentions that about 60 millions "cubic tons" of conifers suitable for turpentine-extraction (*Abies sachalinensis* and others) are available, so that if the supply were depleted to the extent of 600000 tons of wood yearly, it would suffice for a century.

¹⁾ Report November 1908, 141.

²⁾ Oil, Paint & Drug Reporter, 77 (1910), No. 6, p. 9.

If re-afforestation were to be resorted to in the meantime, the supply could be rendered almost inexhaustible.

The steady increase in the consumption of oil of turpentine, in conjunction with the decrease of the pine-forests, has led to the search for substitutes of turpentine. It is well-known that such substitutes as have of late made their appearance upon the market, distillates of petroleum, for instance, have chemically nothing in common with oil of turpentine, and do not possess its valuable properties.

Closely akin to genuine oils of turpentine, however, are the so-called "wood-turpentines" which have been brought into trade chiefly from North America. They are manufactured from waste wood, chips, broken-up pine wood and similar materials, and go by such names as "steamed wood turpentine", "wood pulp turpentine", "stump turpentine" etc.¹⁾ Various manufacturing-processes, including dry distillation and distillation with superheated or normal steam, are in use in this industry.

As a result of the reckless devastation of the pine-forests which has been practised for many years, in particular in the United States, the idea has naturally arisen to distil the tree-stumps which have been left standing, and which are known as "light wood". The stumps which are being used up in America at present have remained in the ground many years after the trunk had been removed, and yield a pine wood which is very rich in resin. It would appear that a chemical process is taking place in these stumps by which oil is formed subsequent to the removal of the trunk, for the oil-yield from new stumps is very slight. This fact would also explain why the oil thus obtained is altogether different from ordinary oil of turpentine, and why the percentage is so high.

The stumps which are mostly employed for distilling purposes are those of *Pinus palustris* (long leaf pine), whence the oil is called "long leaf pine oil". Similar products are brought to market under the names of "light wood oil" and "oil of fir"; while the designations "white" and "yellow pine oil" appear to apply to separate fractions of the oil.

According to E. Teeple²⁾, good commercial long leaf pine oils have a sp. gr. of 0,935 to 0,941. The constants of a sample examined by him were as follow: — $d_{15,5^{\circ}}$ 0,945, $[\alpha]_{D20^{\circ}}$ — 11°, n_D 1,4830. Yellow pine oils examined in our laboratory showed more or less divergence from the values given by Teeple, their sp. gr. varying from 0,941 to 0,954 at 15°, and their rotation from + 6° to — 5°. These variations in the constants are partly due to differences in the material of distillation, which is often derived from more than one species of *Pinus*, and

¹⁾ Comp. Report April 1907, 94; October 1907, 94 and 95; November 1908, 125; October 1909, 119, 121, 124.

²⁾ Journ. Americ. chem. Soc. 30 (1908), 412; Report November 1908, 125.

to the presence of a greater or less proportion of terpenes, especially those of the pinene-fraction.

The above-named oils, which are said to constitute excellent solvents for ordinary varnish-resins, rubber, etc. are also very interesting from a scientific standpoint, because α -terpineol has been detected in them, this being the first time that that body has been found in oils from the *Pinus* species.

We have examined a yellow pine oil of which we give some particulars below. Its constants were as follow: —

d_{15° 0,9536, α_D $-3^\circ 26'$, n_{D20° 1,48537, acid no. 0, ester no. 14,2 (corresponding to 4,9 per cent. ester $C_{10}H_{17}OCOCH_3$), ester no. after acetylation 161,4 (corresponding to 50,5 per cent. alcohol $C_{10}H_{18}O$). Acetylation in xylene-solution according to Boulez¹⁾ gave an alcohol-content of 58%. The bulk of the sample boiled over between 190° and 220° , 5% between 160 and 190° .

The oil was fractionated into several parts. From the last fractions a solid body separated out, consisting of l- α -terpineol. The pure body had a m. p. of about 35° ; $[\alpha]_D$ $-4^\circ 40'$ in a 25% alcoholic solution. The terpeneol was identified by the phenylurethane, m. p. 111 to 113° . Teeple had already shown that this alcohol forms a constituent of the oil, but he had not succeeded in isolating solid terpeneol. The portions which were separated from the solid terpeneol by freezing were carefully fractionated and each fraction examined separately.

Hydrocarbon Fractions.

The constants of the first two fractions in which we had occasion to surmise the presence of hydrocarbons were as follow: —

I. B. p. 160 to 180° , d_{15° 0,8702, α_D $-1^\circ 40'$, n_{D20° 1,47964.

II. B. p. 173 to 197° , d_{15° 0,8941, α_D $-4^\circ 1'$, n_{D20° 1,48151.

These two fractions were split up by careful distillation into several portions, the properties of which showed considerable differences. For instance, the portions boiling between 156 and 160° had a rotation $\alpha_D +10^\circ 20'$; those boiling between 175 and 180° gave $\alpha_D -12^\circ 55'$.

The first fractions contained α -pinene, as shown by the nitroso-chloride (m. p. 105 to 107°), of which the nitrolbenzylamine melted at 123° ; β -pinene, proved by oxidation into nopinic acid, and camphene, of which the presence was shown by hydration according to Bertram and Walbaum's method. The resultant isoborneol had m. p. 208 to 209° . The fractions with b. p. between 170 and 180° consisted chiefly of l-limonene and dipentene. By passing hydrochloric acid gas into the glacial acetic acid solution of the hydrocarbons, a satisfactory yield of dipentene hydrochloride (m. p. 48°), was obtained. This was converted, by splitting off hydrochloric acid by means of aniline, into dipentene (b. p. 178 to 180°). The tetrabromide melted

¹⁾ Comp. Report April 1907, 120.

at 122 to 123°. The tetrabromide which was obtained from the fraction boiling between 175 and 177° was a mixture of limonene- and dipentene-tetrabromide, these two constituents being separable by fractional crystallisation. The portion melting between 103 and 106° consisted of active tetrabromide (limonene tetrabromide), the less easily soluble portion melted at 120 to 123° and proved to be dipentene tetrabromide. By treatment with nitrosyl chloride a nitrosochloride was obtained which could not be identified more closely, either as nitrol-piperidine or as nitrolbenzylamine. This result was to be expected if it is remembered that the piperidine- and benzylamine-compounds both of limonene and of dipentene exist each in two isomeric forms, which circumstance greatly appropiates the difficulty of separating by fractional crystallisation.

We were unable, from the dihydrochloride, to prove the presence of sylvestrene in the fractions boiling between 173 and 180°. This hydrocarbon, which is notoriously a constituent of many pine-tar oils, appears therefore to occur in this yellow pine oil only in very minute proportions, if at all.

On the other hand, the fractions with b. p. 174 to 180° still contained cineol. Our attention was drawn to this compound by the remarkably high density which was displayed by some fractions, notwithstanding repeated distillation over sodium. The cineol was converted into the cineol-resorcinol compound by shaking with resorcinol solution. In the crude product obtained by the decomposition of the impure cineol-resorcinol, cineol was identified by the iodol-compound, m. p. 110 to 112°.

The fractions boiling between 178 and 180° contained small proportions of γ -terpinene. The erythritol which was formed by oxidation with permanganate melted at 232 to 235°. In another portion of the oil, which had been shaken up with dilute sulphuric acid in order to effect the removal of the still remaining α -terpineol we were able, in the course of the examination of the hydrocarbon-fractions, to ascertain the presence of terpinene from the dihydrochloride (m. p. 52°). It is very probable, however, that this larger terpinene content is due to the action of the sulphuric acid.

Alcohol Fractions.

In the course of the various experiments which were undertaken in order to arrive at a knowledge of the separate constituents of the alcohol-fractions, the existence of large proportions of α -terpineol proved to be a very troublesome fact. As this constituent could not be removed by fractionation, the terpineol was converted into terpin hydrate by shaking with dilute sulphuric acid and was separated from the other constituents by distillation with steam. The oil which was thus separated from the terpineol was repeatedly fractionated.

We succeeded in isolating, besides borneol, methyl chavicol, a body which had not previously been observed in oils from the *Pinus*-species.

The residues of the hydrocarbon fractions already contained considerable proportions of borneol, which we were able to detect therein by the acid of borneol-phthalic ester, m. p. 164° . In the fraction boiling between 210 and 215° , which, judging by their boiling point and density were bound to contain particularly large quantities of borneol, we proved the existence of this body, and isolated it, by the following method: — 200 g. of the fraction were boiled for an hour with chemically pure formic acid, in order to eliminate the terpineol. The solution very quickly turned turbid, water being separated. The borneol formiate, purified by fractionation, was saponified with potash. In the course of subsequent fractionation, the borneol separated out in the solid state. Recrystallised from petroleum ether it was laevo-rotatory, and had m. p. 204° . The phenyl urethane melted between 137 and 139° , the semicarbazone of the camphor which was obtained by oxidising with chromic acid, at 237° . Afterwards we were also successful in separating directly from the original oil, by careful fractionation, borneol with a m. p. of 203 to 204° , $[\alpha]_D - 1^{\circ}55'$, in a 20 per cent. alcoholic solution.

In the fractions containing borneol, methyl chavicol was also found to be present, and the two compounds could not be separated by fractionation. A fraction which had already been treated with formic acid was therefore heated on an oil-bath for 4 hours to 160 to 170° with an equal weight of phthalic acid anhydride. By this means the borneol was converted into the acid borneol phthalic ester, and the methylchavicol was then isolated with ether from the aqueous solution which had previously been neutralised with soda. The major portion of the oil boiled respectively between 73 to 74° (4 to 5 mm.) and at 215° (758 mm.). Its constants were: $d_{15^{\circ}} 0,9710$, $\alpha_D - 0^{\circ}27'$, $n_{D20^{\circ}} 1,51726$.

A comparison of this methyl chavicol with a methyl chavicol isolated by us from oil of fennel showed close agreement between the two: —

Methyl chavicol

from Yellow Pine oil	from fennel oil
b. p. 215°	b. p. 215°
$d_{15^{\circ}} 0,9710$	$d_{15^{\circ}} 0,9700$
$n_{D20^{\circ}} 1,51726$	$n_{D20^{\circ}} 1,51884$

The identification of methylchavicol was completed by oxidation into homo-anisic acid. 15 g. methylchavicol was oxidised with 20 g. permanganate and 10 g. acetic acid in 400 g. water under cooling. The concentrated oxidation liquors, after having been acidulated, yielded upon extraction with ether an acid, m. p. 83 to 84° which proved to be identical with homo-anisic acid from methylchavicol obtained from

oil of fennel. A crude fraction, when oxidised with a rather large quantity of permanganate, also yielded anisic acid, m. p. 183 to 184° .

The conversion of methylchavicol into anethol was accomplished by boiling with alcoholic potash. 10 g. Methyl chavicol was dissolved with 15 g. potash in 200 cc. alcohol and heated for three days on the water bath. The alcohol was then distilled off and the residue diluted with water and treated with ether. The resulting product boiled between 230 and 233° and melted at above 15° . The odour of the methylchavicol and the anethol was greatly affected by the presence of traces of borneol.

The isolation of methylchavicol was also carried out by the action of benzoyl chloride upon the fractions with b. p. 210 to 215° . By this process the borneol was converted into the benzoic ester and the methylchavicol recovered by distillation with steam.

The fractions of which the b. p. lay between those of the hydrocarbons and the borneol, and which had not been treated with sulphuric acid had a very peculiar, musty, mouldy odour. They consisted for the most part of fenchyl alcohol. No fenchone could be detected, but from the fractions from which the fenchyl alcohol had been removed a small quantity of a semicarbazone, m. p. 233 to 235° , was obtained by means of semicarbazide hydrochloride. This semicarbazone was identical with camphor-semicarbazone. Only traces of camphor, therefore, occur in the oil.

The method pursued for isolating the fenchyl alcohol was as follows: — The portions boiling between 197 and 204° which had been obtained by repeated fractionation were heated for 4 hours to 150 to 160° on an oil-bath with an equal weight of phthalic acid anhydride, and the product of reaction was then further treated in the familiar manner. Then, upon the addition of acid, crystallised acid phthalic ester, m. p. 142 to 143° , separated out from the aqueous solution of the salt of the acid phthalic ester. When the substance was heated very rapidly, its m. p. was 145° . No acid phthalic ester of higher m. p. was obtained. The alcohol which was liberated by saponification with alcoholic potash was purified by steam distillation; it boiled between 201 and 204° , and had a very persistent mouldy odour. Even when distilled with steam the bulk of the alcohol separated out in the solid form. Its liquid portions were removed by rapid filtration. The m. p. of the solid body which was obtained after repeated purification, as determined in a closed capillary tube, was 33 to 35° , or, when the heating took place very rapidly, 37 to 38° . As regards the constants of the alcohol it may be mentioned that its b. p. was between 202 and 203° and that in a 13 per cent. alcoholic solution it was inactive. The ketone (b. p. 192 to 193° or respectively 193 to 194° ; d_{15}° 0.9501; n_{D20}° 1.47021) which was obtained from the alcohol by oxidation with chromic acid also proved

to be identical with i-fenchone. The oxime of the ketone, when heated quickly, melted at 159 to 160°.

By acting with phosphorus pentachloride upon the alcohol when dissolved in petroleum ether, we obtained a liquid chloride, which was converted by the splitting-off of hydrochloric acid by means of quinoline into a mixture of hydrocarbons, of which the major portion boiled at from 154 to 156° (d_{15}° 0,8687, n_{D20}° 1,47240). By hydration according to Bertram and Walbaum's method i-isofenchyl alcohol was formed, of which the phenyl-urethane melted between 93 and 94°.

From the above it is clear that the solid alcohol with m. p. 33 to 34° is i-fenchyl alcohol.

The fact is of particular interest that this alcohol, which has long been known as a product of the reduction of fenchone, has now for the first time been discovered in an essential oil. Borneol, the product of reduction of camphor, is, of course, a compound which is very frequently found in essential oils, and in the oils of the *Pinus*-species (the pine-needle oils) it also forms one of the most important constituents. The fenchyl alcohol with its mouldy odour strongly reminiscent of rotten wood, is also interesting because it occurs in an oil which has been distilled from tree-stumps that have remained in the soil several years after the trunk of the tree was cut down or broken off. It is therefore not impossible that fenchyl alcohol is always present where old or cut-down tree-stumps emit a musty odour.

We give below a comparison of the constants of the i-fenchyl alcohol isolated from yellow pine oil and its derivatives with those of the same body from i-fenchone: —

Fenchyl alcohol and its Derivatives.

From Yellow Pine Oil					From active Fenchone				From inactive Fenchone			
m. p.	b. p.	d	n_D		m. p.	b. p.	d	n_D	m. p.	b. p.	d	n_D
33 to 35°	202 to 203°	—	—	Fenchyl alcohol	45°	201 to 202°	—	—	33 to 35°	201 to 202°	—	—
—	192 to 193°	0,9501 (15°)	1,47023 (20°)	Fenchone	+ 6°	192 to 193°	0,952 (15°)	1,46337 (17°)	—	—	—	—
159 to 160°	—	—	—	Fenchone oxime	164 to 165°	—	—	—	158 to 160°	—	—	—
142 to 143°	—	—	—	Acid phthalic ester	145 to 145,5°	—	—	—	—	—	—	—
—	154 to 156°	0,8687 (15°)	1,47240 (20°)	Fenchene	—	154 to 156°	0,8660 to 0,8665 (15°)	1,46733 to 1,46832 (17°)	—	154 to 156°	0,8665 (15°)	1,46733 to 1,46832
93 to 94°	—	—	—	IsOfenchyl phenyl-urethane	106 to 107°	—	—	—	94°	—	—	—

In addition to the solid fenchyl alcohol, we obtained from the acid of phthalic ester a liquid alcohol: — b. p. 202 to 203°, $d_{15} 0,9655$, $n_D + 1^\circ 10'$, $n_{D20} 1,47465$. In a freezing mixture this alcohol congealed, to liquify again at normal temperature. Oxidation with chromic acid produced i-fenchone, of which the oxime melted at 159 to 161°. By acting upon the alcohol with phosphorus pentachloride we obtained a chloride which was converted into fenchene when hydrochloric acid was split-off from it by means of quinoline. The principal portion of this fenchene boiled at 154 to 156°. Its constants were as follow: — $d_{15} 0,8669$, $n_D - 2^\circ 38'$, $n_{D20} 1,47056$. From its general properties the alcohol might be regarded as a fenchyl alcohol, but experiments to determine its character by means of the phenyl urethanes were unsuccessful. They resulted in the formation of a urethane, m. p. 94 to 95°, which was readily soluble in petroleum ether. The acid phthalic ester melted at 142 to 144°. When oxidised, the alcohol yielded fenchone, so that it is very probable that the liquid alcohol represents a stereo isomeric fenchyl alcohol, possibly also contaminated by small proportions of borneol which cannot be quantitatively eliminated.

It is well known that when fenchone is reduced to fenchyl alcohol there is formed, besides the solid alcohol, a small proportion of liquid fenchyl alcohol. The surmise expressed by several investigators, that the liquid alcohol represents a racemised *isofenchyl* alcohol, has not yet been established as a fact. As *isofenchyl* alcohol, when oxidised, is converted into *isofenchone*, of which the oxime melts at 82 and 133° respectively, the liquid alcohol also (if the theory referred to above were correct), must contain *isofenchone*, but in every experiment tried by us we obtained from the liquid alcohol by oxidation only fenchone and fenchone oxime.

The results of our investigation of Yellow Pine Oil have shown that, (in addition to the α -terpineol which had already been found by Teeple, and which we succeeded in isolating in the solid state,) the oil contains α - and β -pinene, camphene, l-limonene, dipentene, cineol, fenchyl alcohol, camphor, borneol and methyl chavicol. Among these bodies, cineol, fenchyl alcohol, camphor and methyl chavicol had never previously been found as constituents of an oil from the *Abietæ*.

Marcusson¹⁾, in a series of papers dealing very thoroughly and critically with the present position of turpentine oil research, reviews the methods now in use for the detection of adulterations. In view

¹⁾ Chem. Ztg. **33** (1909), 966, 978, 985. Communications from the Königl. Materialprüfungsamt (Prussian Govt. Office for Testing Produce), Gr.-Lichterfelde, West.

of the importance of this subject, we propose here to refer to these methods at some length.

There is no difficulty in detecting the presence of sophistications such as pine-tar oil, ethylene perchloride, dapentine, and sangajol; but it is less easy to prove the existence of certain other adulterants, such as benzine, pine-tar oil (purified?), resin spirits, benzene and its homologues, carbon tetrachloride and so-called "regenerated turpentine oil", (i. e. residual terpenes of camphor-manufacture), especially when these admixtures only occur in small proportions.

The addition of benzine can be recognised by the reduction of the density, the sp. gr. of pure oil of turpentine being from 0,865 to 0,875, and that of the benzine fractions with a b. p. of 100 to 180°, such as are commonly used for sophistication, 0,73 to 0,80. There is also a difference in the indices of refraction: turpentine oil 1,471 to 1,4735, benzine 1,419 to 1,450. According to H. Herzfeld, the addition of benzine may be ascertained by fractional distillation; when, in the case of pure oil, there is but little deviation between the indices of the separate fractions, while portions containing benzine show considerable differences. According to Utz, the refraction should be determined of the portions which have remained undissolved with Herzfeld's sulphuric acid method. In the case of pure oils of turpentine this is 1,492 to 1,499, where as in oils with 10% of benzine it goes up to 1,454.

Pine-tar oil, according to Herzfeld, may be detected by the fact that, where it is present, it very quickly coats a small piece of potassium hydrate with a yellowish-brown layer. When the oil is pure a somewhat considerable time elapses before such coating is formed. Old, resinified oils should be distilled (by steam?) before this test is applied. An admixture of not less than 10% of pine-tar oil may be detected by Herzfeld's sulphurous acid reaction¹⁾ (greenish-yellow coloration), but purified pine-tar oils do not respond to this test. By purified oils are understood such as have been rectified, say, by the method of Kaas (first, treatment with aqueous [earthy] alkalies, afterwards with alcoholic potash-liquor). But, in Marcusson's opinion, pine-tar oils which have been so refined may perhaps be regarded as coming very near to genuine oil of turpentine.

Resin-spirits can be detected by the low point at which it commences to boil (below 150°), and also by Grimaldi's test, viz., the turning green in the presence of a grain of tin and concentrated hydrochloric acid, of that portion of the oil which, after being decomposed into fractions of 3 cc. each, boils at 170° or less²⁾.

¹⁾ Comp. Report April 1905, 78.

²⁾ Comp. Report April 1908, 105.

Benzene and its homologues, solvent naphtha, and heavy benzene lower the bromine number (normally 2,15 to 2,3) of oil of turpentine. According to Herzfeld, admixtures of this description are also traceable by treating 10 cc. oil with 30 cc. concentrated sulphuric acid and cooling with water. Pure oils are said, under this test, to dissolve down to 1 cc.; if a larger residue remains, (which, however, is almost wholly dissolved by subsequent shaking with fuming sulphuric acid,) the presence of benzene hydrocarbons is to be regarded as highly probable. But a check-test of this method showed that it yielded no sharply-defined results. It is true that, when cold, benzene and its next homologues are but little affected by concentrated acid, but when considerable quantities of oil of turpentine are present, complete sulphonisation may easily supervene, in which case the residue is not larger than in the case of many pure oils. Utz'¹⁾ method for the detection of "benzene preparations" on the basis of the refraction of the insoluble parts obtained by the application of Herzfeld's test is not reliable. On the contrary, in view of the fact that Utz observed a lower refraction of the residue, whereas all homologues of benzene show a higher refraction, is it to be suspected that his oils contained certain proportions of benzene.

Marcusson has made a systematic investigation of the effect upon the refraction of oil of turpentine of additions of 10% of the various hydrocarbons of the benzene series, and of the degree to which this effect finds expression in the separate fractions of such mixtures. Whereas in the case of pure oils the refraction of the separate portions increases slowly but steadily, oils to which 10% of benzene compounds have been added show a more or less clearly defined declension of refraction. Only in the case of solvent naphtha is this declension followed by a pronounced increase at the close. The extent of these variations is graphically shown in several tables.

Carbon tetrachloride which, on account of its high density, is added to disguise the admixture of benzene, may be easily traced by Beilstein's copper-test, as well as by the elimination of potassium chloride during boiling with alcoholic potash, and also by fractionation. For quantitative determination, in addition to oil of turpentine and benzene, the chlorine-content of the mixture is ascertained according to Carius: pure tetrachloride of carbon contains 92,2% Cl.

"Regenerated" oil of turpentine, which is obtained as a by-product in the manufacture of synthetic camphor from American oil of turpentine, has not been described in chemical literature up to the present. Two samples of this oil, compared with pure American oil, were found to possess the following properties: —

¹⁾ Comp. Report October 1905, 67.

Sample	External appearance (layer of 6 cc. thickness)	d_{15}°	n_{D15}°	α_D	Bromine No.	Behaviour on treatment		Behav. on of Boiling			
						with — 10° cold HNO_3	with conc. and afterwards with fuming H_2SO_4 (Herzfeld), % of insoluble matter	Commen- cement of boiling	155 to 162° /o (about)	162 to 165° /o (about)	165 to 175° /o (about)
American oils of turp.	thin, water white to yel- lowish, slight odour	0,865 to 0,875	1,4710 to 1,4735	mostly + 9° to + 14°	2,15 to 2,3	com- pletely soluble	1 to 11	155°	75 to 80	20 to 25	
Regen- erated turp. oil (a)	thin, pale yellow, slight odour of oil of turp.	0,8738	1,4788	+ 6,7°	2,04	ditto	14	164°	—	10	75
Regen- erated turp. oil (b)	ditto, but with disagreeable subsidiary odour	0,8559	1,4762	+ 0,08°	1,8	ditto	13	170°	—	—	100

It follows from the above that regenerated oil differs from pure oil in its higher rotation, lower bromine number, higher content of constituents insoluble by acid and much higher b. p. In addition to this the two samples of regenerated oil differed from each other, these differences being perhaps due to variations in the camphor-processes. Marcusson regards the presence of such oils as probable in cases where less than 75 to 80 % of the sample have passed over at 162° in the course of distillation (that being the percentage of pure oil of turpentine), and where other tests have shown the absence of benzene, benzine, pine tar oil, etc.

For the detection of benzine, the most frequently employed adulterant of oil of turpentine, (many "oils of turpentine" consist principally of benzine), Burton's test to be applied in Herzfeld's apparatus¹⁾, was originally recommended. In this test the sample of oil was treated with fuming nitric acid, under cooling by water, the undissolved portion being regarded as benzine. But the test which had first been recommended by Herzfeld in this form was subsequently abandoned by him in favour of the sulphuric acid process (of which he was also the originator), because it was found that the gases generated during the reaction carried off benzine vapour. Moreover, Herzfeld found that in cases where the acid reacted violently upon the oil, explosions were apt to occur at times. But check-tests, made in the Govt. Office for Testing Produce (*Materialprüfungsamt*) show that the sulphuric acid method, which is said, when applied to pure oil, to leave at most 2 % undissolved, is equally unworthy of recommendation, inasmuch as it has two serious drawbacks. In the first place it has been found that many pure oils of turpentine, even after being treated twice with sulphuric acid, showed a much larger percentage of insoluble matter than was stated by Herzfeld. In two cases of pure

¹⁾ Comp. Report April 1904, 85.

oils the insoluble residue amounted to 10 and 11% respectively; pine-tar oils left from 3,5 to 8%; resin-spirits as much as 20% of insoluble matter. Secondly, the sulphuric acid decomposes not only the oil of turpentine, but also powerfully attacks the benzine. Of the constituents of benzine, viz., hydrocarbons of the paraffin series, naphthenes, aromatic hydrocarbons and olefinic hydrocarbons (the last-named forming a minor proportion), the aromatic and olefinic constituents are dissolved by the acid. From 10 to 41% of the benzine, according to the origin of the substance, are soluble. These two faults, as already shown by Coste¹⁾, have opposite effects and may mutually cancel each other. Of the methods at present known for detecting the presence of benzine, the best is Burton's modified test, which consists of treating the oil-sample with fuming nitric acid at -10° . In this acid all oils of turpentine and pine-tar are completely soluble; resin-spirits although not completely soluble, only leave a residue of up to 1,5%, which indicates a small naphthene-content. One drawback of the nitric acid test is that the olefinic and aromatic constituents of benzine are also dissolved, and that therefore the benzine content comes out too low. Careful experiments with benzine distilled from crude petroleum oils of different origin and with commercial benzines, afford an indication of the wide differences in the degree of solubility of various benzines both with Herzfeld's and with the modified Burton-method. American and Russian benzines showed the smallest proportion of soluble matter (8 to 10%), next came Galician (15 to 20%), while East-Indian benzines from Sumatra and Borneo ranked highest, viz., from 22 up to 41% according to the boiling-temperature.

Under Burton's test, benzine when mixed with oil of turpentine loses about the same percentage proportion as does pure benzine, provided that the benzine greatly exceeds the oil in the mixture; say 70% benzine and 30% oil of turpentine. When the benzine-content is smaller (say 10 to 20% only), there is a loss of benzine owing to the more radical action of the acid, and this loss may amount to as much as 43% of the total quantity of benzine. As it might well be assumed that the aromatic constituents of benzine were converted into nitro-compounds insoluble in water, whereas the olefines, which only exist in small proportions, were oxidised into bodies soluble in water, the following test was applied after several preliminary experiments: The oil-sample was treated in the familiar manner with nitric acid in a specially constructed apparatus (see below), and after reading-off the unaffected volume of oil the total liquid was passed through a separating funnel. The acid was poured into 150 cc. water and warmed for about a quarter an hour on a steam bath in a draught-cupboard.

¹⁾ Comp. Report October 1909, 125.

Cloudiness ensued, and under liberation of a plentiful volume of re vapours, an oil separated out. The solution was then left to cool and the oil extracted with ether. The ethereal solution was first washed with water, next with a potash solution of about 8% (50 g. potassium hydrate, 500 cc. water and 50 cc. alcohol), and finally again with water. It was then dried with calcium chloride and evaporated. As the mean specific gravity of the residue, which consists of the aromatic nitro compounds, may be taken at 1.15, the weight of the residue was divided by that figure and the resulting volume-number added to that which had been read off direct. The practicability of this method was demonstrated by a series of tests with oil samples from various kinds of benzine, the effect of the treatment upon each variety of benzine being shown by figures. Hence in certain circumstances such as a small content of oil of turpentine, the quality of the benzine may be concluded from the constants of the residual body.

Further communications and tables relate to the properties of the principal benzines of commerce, their constitution, (paraffins, naphthenes, olefines and aromatic constituents), and their consequent variations of behaviour under the sulphuric and nitric acid tests. Another table demonstrates the influence of the treatment with each of the acids upon the constants of the separate benzines as compared with the original preparation.

In an appendix, Marcusson and Winterfeld describe an apparatus for applying the modified Burtontest. The essential parts of this apparatus are a round flask with a long, graduated neck, and, fused into the latter, a separating-funnel of precisely 10 cc. capacity. The fuming acid is first poured into the flask, which is then cooled down to -10° . Next the oil-sample is slowly introduced through the funnel, this taking from 30 to 60 minutes. At the conclusion of the reaction the oil which remains intact is driven into the graduated neck of the flask by the addition of concentrated acid, and its volume read off there. The oil and the acid are then separated in another separating funnel and the acid is treated further as described above.

Herzfeld¹⁾ takes the field against Marcusson's criticism of his sulphuric acid process. He explains the divergence of Marcusson's results from his own by insufficient cooling during the test, and points out that Marcusson has used considerably larger proportions of acid than is proper. Herzfeld also takes exception to the description "regenerated oil of turpentine" as applied to the waste terpenes in camphor manufacture, for the detection of which the high degree of separation of the oils treated with sulphuric acid is important. Apparently the oils of turpentine which were regarded as pure by Marcusson, and

¹⁾ Chem. Ztg. **33** (1909), 1081.

which gave a sulphuric-acid residue of 10 to 11%, were in reality adulterated with such waste terpenes. With normal oils of turpentine the inaccuracies of the nitric acid process are always greater than those of the sulphuric acid process, but in doubtful cases, as, for instance, where carbon tetrachloride is present, Burton's process may also be applied. Where this is done it is desirable to warm the insoluble portion with fresh nitric acid up to 50 to 60°, when all the carbon tetrachloride goes into solution. Herzfeld has not met with any pine-tar oils which, after being purified by Kaas' method, failed to respond to the sulphurous acid test. The apparatus constructed many years ago by Herzfeld, which serves the same purpose, differs from that described above only by the very practical addition of a fused-in thermometer.

Vaubel¹⁾ was the first investigator who recommended the observation of the behaviour of oil of turpentine towards bromine, and of the absorption of the bromine by the oil for the purpose of estimating the value of the latter, but his suggestions have not been allowed to pass without contradiction. On the same principle Mansier²⁾ tests the petroleum-hydrocarbon content of the oil. He shakes up 1 cc. of the oil sample in 5 cc. chloroform with as much 3 per cent. aqueous solution of bromine until no further decoloration ensues. Pure oils, when treated in this manner, used up 1,69 g. bromine = about 60 cc. of the bromine solution; when petroleum is present this figure undergoes a proportionate decrease. In order to determine the percentage proportion, the bromine solution is compared with a solution of sodium formate (1,6125 g. per litre). The bromine-number (that is to say the weight in grammes of bromine absorbed by 1 g. of the purest oil of turpentine) given by Vaubel was 2,2 to 2,3; Marcusson, in his paper referred to above, gives it as 2,15 to 2,3; according to Mansier the bromine number calculated for weight, (given turpentine oil of 0,86 sp. gr.) is 1,96.

It is evident that the experts disagree as to the value of even the oldest and most thoroughly-established chemical tests. In view of this fact it is worth while to call attention to investigations concerning the physical properties of oil of turpentine in admixture with other bodies.

In the laboratory of Vèzes, Queysanne³⁾ has investigated the reciprocal solubility of French oil of turpentine and of aniline. His

¹⁾ Comp. Report April 1906, 66; October 1906, 77 and 78.

²⁾ Annales de la chim. analyt. appl. 14 (1909), 417; Through Zeitschr. f. angew. Chem. 23 (1910), 46.

³⁾ Sur la solubilité réciproque de l'essence de térébenthine et de l'aniline. Bordeaux 1909. From a reprint kindly sent to us.

method consisted in taking mixtures of varying proportions and determining the temperature at which separation commences. The values thus ascertained were entered on a table of co-ordinates, the ordinate standing for the percentage proportions of the two substances and the abscissæ for the temperatures. The melting-curve of the aniline turpentine oil mixture was plotted on a similar plan.

According to one of the Regulations of the Prussian Excise Authorities¹⁾, the solubility of oil of turpentine in an equal volume of aniline is used as a test to determine the presence of "Patent turpentine oil", on the ground that oil which has been sophisticated with this adulterant does not give a clear solution, but apart from this, the above-named test can hardly be said to be of any practical account.

Nicolardot and Clément²⁾ believe that additions of petroleum white spirit, resin oil, etc. to oil of turpentine may be detected by means of the difference in rotation in the oil-fractions when distilled under a vacuum of 18 mm. (not cm.!), and also by means of the flashpoint, which is known to be slightly lowered by petroleum distillates, and somewhat increased by resin oil. They also invoke the assistance of the differences in the behaviour of turpentine oil when evaporated in atmospheric air in the light and in the dark. In the case, when the adulterants referred to are present, the rotation before and after evaporation is changed in a different way from that of pure oils.

The explanations of the authors are partly contradicted by the figures in their tables, and in various places the paper gives the impression of careless editing.

When the residue of evaporation of oil of turpentine is determined in the customary manner by heating on the water bath, the values found are too high, because at waterbath-temperature the oil oxidises most rapidly and becomes resinified to a not inconsiderable extent. For this reason H. Herzfeld³⁾ determines the residue of evaporation in the neighbourhood of the boiling-temperature of the oil by embedding a platinum-dish up to the rim in a sand-bath, heating it to 155°, and then slowly adding 5 cc. of oil. When the steam has ceased to evolve the heating is continued for another 15 minutes. The results of various experiments showed but slight

¹⁾ Chem. Ztg. **22** (1898), 834. Gildemeister and Hoffmann, *The Volatile Oils*, p. 235.

²⁾ Compt. rend. **49** (1909), 572.

³⁾ Chem. Revue Fett- und Harzind. **1909**, 174; through Pharm. Zentralh. **5** (1910), 72.

discrepancies; but there is a very marked difference between the figures obtained by this process and those of the water bath method.

Kollo¹⁾ altered the *modus operandi* of Herzfeld's experiment by surrounding the platinum (or nickel) dish with a ring of tin of about one finger-width. This suggestion was made by Guigues, and the object is to prevent the ignition of the suddenly-generated turpentine-vapours. The ring, where it touches, induces strong evaporation; each drop evaporates at once, and the object of the experiment is attained more quickly and surely. The platinum dish must project free from the ring only to the extent of a very narrow margin; it is embedded in the sand-bath up to the ring, heated to 155° and the oil is added very slowly (100 drops a minute), from a separating funnel which has been twice bent at right angles and is drawn out to a tapering point. The results of four experiments made by this modified process agreed mutually. When the tin-ring was omitted the oil of turpentine, in one experiment, caught fire.

Some time ago²⁾ we made a brief reference to an investigation by Darmois, in which an attempt was made to ascertain the constitution of oils of turpentine by the aid of rotatory dispersion. In the course of his investigations, Darmois succeeded in establishing the presence, in the fraction of a dextrorotatory oil boiling between 155 and 163°, of a strongly dextrorotatory (d-pinene), and a faintly lævorotatory portion. By applying the same process to a lævorotatory oil of turpentine which had been split up into 20 fractions, Darmois³⁾ found that this oil was composed, in a similar manner, partly of a strongly and partly of a faintly lævorotatory hydrocarbon. That the latter was identical with that of the oil previously examined, was inferred from the fact that the rotation $[\alpha]_D$ was the same, viz., about $-21,7^\circ$. As Darmois, like Vèzes, had isolated from the oil of the Aleppo pine about 90% of a d-pinene with the rotation $[\alpha]_D +48^\circ$, (m. p. -50°) it was inferred, from these optical constants, that the oil in question contained 62% of l-pinene and 38% of the new, slightly lævorotatory body. Darmois believes the last-named body to be nopinene, notwithstanding the fact that oxidation yielded only a very small proportion of nopinic acid. The figures ascertained for rotatory dispersion were in the case of d-pinene from Aleppo pine oil $\frac{\alpha_\lambda = 436}{\alpha_\lambda = 589} = 2,02$. No value is quoted for the other hydrocarbon.

¹⁾ Ibid. 154.

²⁾ Compt. rend. 147 (1908), 195; Report November 1908, 124.

³⁾ Compt. rend. 149 (1909), 730.

A recently-published American Consular Report¹⁾ contains further information on the subject of the "electrical" manufacture of "oil of turpentine", which may be quoted in continuation of our previous communications²⁾. Picked waste material from the saw mills produces per cord of wood from 6 to 8 gallons of distilled oil, but a considerably richer yield was obtained from the pine-stumps, varying from 6 to 8 feet in height, especially from the stumps of the Douglas pine and of trees growing at higher altitudes which had been thrown down by the wind, and of which the lower portion of the trunk is extremely rich in resin and has no timber value. The balance sheet of the undertaking, which is also reproduced, is favourable, and the managers declare themselves most satisfied as to the quality of their product in comparison with the "frequently adulterated" commercial oil of turpentine.

The only terpenes of resin-spirits which were known up to the present were pinene and dipentene. Recently, however, C. Grimaldi³⁾ has examined two resin-spirits obtained by dry distillation from Austrian and American colophony. Having first carefully fractionated them over sodium, the author was able, in the fraction with b. p. 155° to 157°, to prove the presence of α -pinene, which he identified from the nitrol piperidin as well as by its constants ($[\alpha]_{D20}$ for pinene from Austrian resin-spirits, $-26^{\circ}10'$, and for pinene from American resin-spirits $+2^{\circ}5'$). By means of Bertram and Wallbaum's hydration method, Grimaldi proved in both spirits the existence of camphene (m. p. of the bromal compound of isoborneol 71 to 72°). Neither sylvestrene nor phellandrene were found present. On the other hand the author was able to prove the occurrence of dipentene, which could easily be detected in both samples by the tetrabromide (m. p. 124 to 125°) and by the constants.

Pikos⁴⁾ has observed a peculiar phenomenon in connection with the vapour of oil of turpentine (pine-tar oil), which is probably due to zoo-physiological causes. When driving a carriage and pair he noticed that whenever he approached a stock of oil-saturated barrels containing crude or partly purified pine-tar oil, or whenever he passed a works where such oil was distilled, even at a distance of over a quarter of a mile, a thick white vapour ascended with great rapidity from the backs of the animals, the skin of the horses generally remaining quite dry. Pikos traces the chemical cause of the occurrence to the forming of compounds from certain constituents of the pine-tar

¹⁾ Daily Consular and Trade Reports, 11th Nov. 1909, p. 5.

²⁾ Comp. Report October 1909, 119.

³⁾ Chem. Ztg. 33 (1909), 1157.

⁴⁾ Zeitschr. f. angew. Chemie 22 (1909), 2235.

oil vapours with the ammoniacal exhalations of the animals. A letter to the Editor of the paper in which the statement appeared¹⁾ points to the probability that the phenomenon has a physical cause, and suggests that condensation-inducing bodies are formed within the slowly oxidising exhalations of the oil, which in their turn cause the formation of the white vapour.

We regard it as quite as likely that a chemical process is set up by the ammoniacal animal exhalations and the air in the neighbourhood of the oil-distilleries, which most probably is charged with acetic acid vapours.

Vèzes²⁾, in his laboratory specially equipped for turpentine-research, has examined Algerian oil turpentine, the product of the Aleppo-pine, *Pinus halepensis* Mill., which is also the parent-plant of the Greek oil. He states that the tree in question occurs plentifully in Algeria, and is also found in certain parts of Southern France. A carefully collected sample of the gum yielded 27% oil; 66,7% dry resin; 0,8% impurities; samples of less purity contained only 14,7 to 17,3% oil; 71,9 to 78,3% of a darker-coloured rosin; and 4,9 to 6,6% impurities. The oils which were obtained from the above and two other samples possessed the following constants: d_{25° 0,8552 to 0,8568, $[\alpha]_D + 46,6$ to $+ 47,6^\circ$, n_D 1,4638 to 1,4652. Upon fractionation 80% of the oils passed over between 155 and 156°, showing the following properties: d_{25° 0,8541 to 0,8547, $[\alpha]_D + 47,4$ to $48,4^\circ$; n_D 1,4633 to 1,4639. With the exception of the density, these values are in close agreement with those given by Tsakalotos³⁾ for Greek oil, and likewise, also as regards density, with the values observed by other investigators in pure pinene. It is probable, therefore, that the oil in question consists to the extent of about 80% of pure d-pinene. The value $[\alpha]_D + 48,4^\circ$ given by Vèzes is the highest on record, and compares with $+ 46,73^\circ$ as the highest value ascertained by us⁴⁾.

The properties and constants of the distillates of *Pinus halepensis* Mill., as observed by several investigators, including ourselves, are in pretty fair agreement with each other (see above), but an oil which has been distilled by Fernandez⁵⁾, it is said from Spanish Aleppo-pine oil, and rectified over carbonate of potassium, showed the exceptional rotation $[\alpha]_D - 8,73^\circ$, while as regards density, and refraction it possessed normal values, viz., d_{20° 0,859, n_D 1,4654. Hence, Fernandez' oil is not identical

¹⁾ Ibidem 2427.

²⁾ Bull. Soc. chim. IV. 5 (1909), 931.

³⁾ Comp. Report November 1908, 121.

⁴⁾ Report October 1909, 69.

⁵⁾ Paper read before the Spanish Physical and Chemical Society, 8. Nov. 1909. According to Chem. Zeit. 33 (1909), 1341.

with oil from Aleppo-pine, nor with the ordinary Spanish oil of turpentine. That there was no question of pure α -pinene, such as is usually found in Aleppo-pine oil, was evident from the result of treatment with dry hydrochloric acid gas, when only 35 to 40% of solid, and 60 to 65% of liquid mono-hydrochlorides were obtained. Both of these by means of magnesium and subsequent steam-distillation, (said to have been carried out by Hesse's method) were convertible to the extent of 88 to 92%, into borneol and further on into camphor. The m. p. of the borneol is given at 115 to 116°, the "specific" rotation of its 5 per cent. alcoholic solution at -10° . We have no doubt that, if Fernandez should continue his investigation, and perhaps repeat his experiments, he will not be able to confirm the values now given by him. Moreover, in following Hesse's method of obtaining borneol from pinene hydrochloride, it may be necessary to oxidise the magnesium compound prior to the treatment with steam.

According to observations made by Richmond¹⁾, a variety of *Pinus* (*P. insularis* Endl.) which occurs in the Northern part of the Philippine Island of Luzon, in the Province of Benguet, and which closely resembles the American *P. ponderosa* Dougl. and the Indian *P. Khasya* Royle, yields a gum of the appearance of granulated honey, possessing a pleasant odour. From this gum he obtained by steam distillation 23.4 per cent of a water-white turpentine oil, possessing the following constants: $d_{30^\circ}^{30^\circ}$ 0.8593, $n_{D30^\circ}^{30^\circ} + 26.5^\circ$, n_{D30° 1.4656; 96% of the oil passing over between 154 and 165.5°. The residual rosin, when filtered, left only 1% of impurities, and the filtrate was of a very pale colour and good quality. The gum was obtained from the tree by the "box"-method. By using the more economical "cup-and-gutter" method the yield of gum could probably be increased, owing to the avoidance of waste.

For the determination of d- α -pinene in certain oils of turpentine, see "pinene", p. 167.

Vetiver Oil. A sufficient selection of crude material from various sources has been available for preparing the exquisite oil distilled by ourselves. The prices, however, have remained unchanged, because this quality in particular was greatly in demand. In the Island of Réunion, the over-production, of which complaint has already been so frequently made, is still increasing, and as a result it is not surprising that at the low prices ruling (which there is even some difficulty in obtaining) the producers are quite unable to make a profit. The oil is being offered on the spot at 25 frs. per kilo first cost, but

¹⁾ Philippine Journ. of Sc. 4 (1909), A, 231.

without encountering even a moderate demand. The shipments in December 1909 amounted to 223 kilos, which brings the total exports of the year up to 1861 kilos, compared with 1025 kilos in 1908. Nothing is being heard of any large transactions in the chief centres in Europe, and it is therefore to be feared that the bulk of these important supplies will accumulate somewhere in anticipation of more favourable times, — just as is the case with Réunion geranium oil.

Wormseed Oil, American. We have repeatedly, in these Reports¹⁾ referred to the valuable properties of American wormseed oil (*Oleum Chenopodii anthelmintici*) as a remedy for ascarides. We have again received medical testimony to this effect quite recently. The remedy had been prescribed as follows: —

R/. *Oleum Chenopodii anthelmintici* 2,5, *Oleum Ricini* ad 100, m. d. s. one tablespoonful to be taken three times every morning at 8, 9 and 10 a. m. The worms passed off at the latest in the forenoon of the second day, but usually within from 5 to 7 hours, in one case between 70 and 80 at a time. Special stress is laid upon the fact that no disagreeable after-effects have ever been observed.

This oil has secured a regular sale on the European market, and we shall at all times be pleased to supply medical men, who are interested in the article with, samples as well as with literature relating to its employment.

Wormwood Oil. Owing to the increased production of this oil in America, to which reference was made in our last Report, no upward movement in the prices was reasonably to be expected. Nevertheless in the course of the autumn it was shown that the shortage of French distillate was having a more considerable influence upon the market than had been at first surmised. Hence the American output quickly found buyers at rising prices, and in the course of the winter the value advanced from about \$ 5,50 to \$ 6,50 per lb., at which latter figure it appears to be maintaining itself. The residue of the stock is being kept back by wealthy holders, higher prices being confidently expected in the course of the next few months. For our German wormwood oil we have experienced a very heavy demand on account of its unapproached quality, and it will be our endeavour, by suitable enlargement of our cultivations at Miltitz, to obtain in the future for our manufacture a position in which it will be able to have its say in the determination of prices. French oil has only been offered sporadically, and in almost negligible quantities. In this case the oil was frequently of a quality which had been heavily adulterated with spike oil, and which had been kept in stock for some time, the existing scarcity inducing holders to try to place it at favourable rates.

¹⁾ Report October 1906, 81; April 1907, 102; October 1907, 99.

These sporadic offers, however, do not in any way alter the fact, to which we have already called attention on previous occasions, that French wormwood oil has ceased to count as a commercial article.

Ylang-Ylang Oil. Our well-known "Sartorius" brand has suffered less than others from the slowness which has recently characterised the ylang-ylang market, for it has numerous friends who always give the preference to this excellent quality when in need of a fine oil possessing a specially excellent *bouquet*. In the course of last summer considerable quantities accumulated owing to the slackness of business, but during the winter these have been reduced, and we are expecting the arrival of new shipments with some impatience. The "Sartorius" brand is particularly esteemed in France, which is a matter of some significance in view of the fact that on patriotic grounds French buyers would be inclined to prefer the oil from the French colony of Réunion, which in the course of the last few years has constituted such an abundant source of supply. The latest statistics available go to November 30th 1909, up to which time the shipments from St.-Denis amounted to 1810 kilos, compared with 1126 kilos in the corresponding period of 1908, thus showing again a considerable increase. We greatly doubt whether the whole of this quantity, in addition to the supplies from Manila, has gone into consumption. We must again express a fear that the senseless increase in the production will render an ill service to all parties concerned in the business.

Tassilly¹⁾, in the *Bulletin des Sciences Pharmacologiques*, reports on the cultivation of the ylang-ylang plant in Réunion. As we have already dealt with the matter in previous Reports²⁾, we need only mention the paper here in passing. Tassilly, in conjunction with Leroide, has examined a sample of Réunion ylang-ylang oil, which had the following constants: d_{15° 0,939, α_D — 64° , n_{D20° 1,510, sap. no. 97. The oil was found to contain: benzoic acid 9,05%, acetic acid 4%, alcohols (linalool and geraniol) 25,50%, cadinene 31%. The authors unfortunately omit to state how each constituent was determined.

New Essential Oils.

Oil of Cinnamomum Tamala. Besides other low-grade *Cinnamomum*-species, it is especially *Cinnamomum Tamala* (Nees et Eberm.), a tree of medium size, growing plentifully in Southern Asia,

¹⁾ Bull. des Sciences Pharmacologiques **17** (1910), 1; from a reprint kindly sent to us.

²⁾ Flacourt, Revue des cultures coloniales **13** (1903), 366; **14** (1904), 16; Report April 1904, 89; also compare Report November 1908, 128; October 1909, 130.

which yields "Mutterzimt", *Cassia Lignea*, or Woodcassia, termed by the detail trade simply *Cassia*. The leaves of the tree are still used medicinally in the East Indies; in former years they were also met with in commerce (the narrow *Folia Malabathri*) but they are now obsolete. The leaves contain an essential oil of which we recently received a sample, which had been distilled by Mr. I. H. Burkill, of Calcutta. The oil was of a lemon-yellow colour, and had a clovelike, at the same time slightly peppery, odour. It possessed the following constants: d_{15° 1,0257, $\alpha_D + 16^\circ 37'$, n_{D20° 1,52596; phenol-content 78%, soluble in 1,2 volumes and over of 70 per cent. alcohol. The phenols consisted of eugenol (m. p. of the benzoyl compound 69°). When freed from phenols, the oil had the high optical rotation $\alpha_D + 66^\circ 40'$ and yielded a solid nitrite which, when recrystallised from ethyl acetate melted at 113 to 114° . It contained therefore d- α -phellandrene. In respect of its high eugenol content it is closely allied to the ordinary oil from Ceylon cinnamon leaves.¹

Guayava Oil. The guayava tree (*Psidium Guayava* Raddi, Myrtaceæ) is a native of tropical America and bears fleshy berries which are eaten both in the raw state and as a preserve. The leaves, when chewed, are said to be a remedy in toothache, and, according to Altan¹), contain 0,36% of an essential oil with a sp. gr. d_{15° 1,069 and a boiling-point of about 237° .

We have recently received an oil of guayava leaves from Santiago de Cuba, which had been obtained from the raw material to the extent of 0,2%. It was of a lemon-yellow colour and had a faint aromatic odour. We found it to possess the following constants: d_{15° 0,9157, $\alpha_D - 10^\circ 5'$, n_{D20° 1,49638, acid no. 2,0, ester no. 6,4, soluble in about 10 volumes of 90 per cent. alcohol.

Oil of *Mentha silvestris*. An oil of *Mentha silvestris* L., prepared in Cyprus, was found to possess the following properties: d_{15° 0,9701, $\alpha_D + 31^\circ 30'$, n_{D20° 1,49544, acid no. 2,4, ester no. 20,9, ester no. after acetyl. 171,4, soluble in 3 vols. of 70% alcohol; (the diluted solution showed slight opalescence;) faintly mint-like odour; yellow colour. It is obvious that the saponification number of 171,4 after acetylation of the oil cannot in this case be indicative of the menthol content, which, judging by this factor, should have been 54,8%; for as a matter of fact the sample contained but little menthol. The mint-like odour was chiefly due to the presence of pulegone, of which the oil contained 40% (isolated with neutral sulphite of sodium). In addition to this a phenol (probably carvacrol) could be detected, from which it is to be supposed that this, also, would become esterified and

¹) L'Union Pharmaceutique 1904, 494. Through Chemist and Druggist 66 (1905), 14.

would help to swell the acetylation value. Owing to the simultaneous occurrence in it of menthol, pulegone and a phenol, the oil cannot be used either as peppermint oil or as european pennyroyal or origanum oil. It is differentiated from oil of peppermint by its much higher specific gravity and by its pronounced dextrorotatory power. We received the sample from the Imperial Institute in London.

Pharmacopœias.

Hungarian Pharmacopœia.

(Pharmacopœa hungarica ed. III.)

The second edition of the Hungarian Pharmacopœia, which has been in force since 1888, having been replaced by a new edition on January 1st 1910, we avail ourselves of this opportunity to discuss its contents, so far as they relate to our branch of industry, in the manner customary with us as regards new Pharmacopœias.

Very little advantage indeed has been taken of the scientific progress of the last 22 years in the domain of essential oils; as in previous editions, the principal points considered are colour, odour, specific gravity and solubility, although in many cases more thorough tests would have been desirable. Moreover, in the present edition certain obsolete tests (for instance the iodine-test) are perpetuated which are without any value in judging essential oils, and which for this reason have been left out of account in the criticism which follows.

Newly incorporated are menthol and neroli oil, while of the oils which were previously official, the following have been struck out, viz., rectified oil of amber, mace oil, marjoram oil, orange oil, rosemary oil, spearmint oil and valerian oil.

As regards alcohols, the Pharmacopœia enumerates a *spiritus concentratus* of 89,8 to 90,1 per cent. by volume and a *spiritus dilutus* of 69,8 to 70,2 per cent. by volume.

We now refer to the various oils and preparations thereof: —

Anise Oil, Russian (*Oleum Anisi*). Colourless or faintly yellowish: neutral reaction; $d_{15} 0,980$ to $0,990$ ¹⁾; solidifies at about $+9^{\circ}$, but at 15 to 19° again becomes liquid and clear²⁾; soluble in 1,5 to 5 vols. *spiritus conc.*³⁾; when ferric chloride is added the solution must not turn violet.

¹⁾ It is advisable to take the sp. gr. at 20° , because anise oil sometimes solidifies of itself at 15° ; the limits of value remain unaltered.

²⁾ It would have been better if, in lieu of this requirement, a definite solidifying point had been laid down; this, in the case of a good oil, lies between $+17$ and $+20^{\circ}$; when the oil is badly kept, or after frequent melting, it is considerably lowered. Comp. Report October 1904, 42.

³⁾ Anise oil is soluble in 1,5 to 3 vols. of 90 per cent. alcohol.

Camphor (*Camphora*). A white translucent and crystalline mass, colourless when in a thin layer. Volatilises without leaving a residue; d_{12}° 0,995¹⁾; m. p. 175°; b. p. 204°; dissolves sparingly in water, readily in *spiritus conc.*, ether, chloroform, fatty and essential oils; the alcoholic solution is dextrorotatory.

¹⁾ The Pharmacopœia is silent as to the manner in which this difficult determination is to be carried out.

Cassia Oil (*Oleum Cinnamomi Cassiae*). Yellow or brownish; neutral reaction¹⁾; d_{15}° 1,055 to 1,065²⁾; soluble in any proportion in *spiritus conc.*; ferric chloride and nitric acid tests; the oil must not solidify when shaken with concentrated soda solution.

¹⁾ Cassia oil is always faintly acid; acid no. 6 to 20.

²⁾ The higher limit of value is too low; it should be 1,070.

Clove Oil (*Oleum caryophyllorum*). When freshly prepared it is colourless or yellowish and gives a neutral reaction¹⁾, by exposure to light and air it turns yellow to reddish brown and acquires an acid reaction; d_{15}° 1,041 to 1,060; soluble in any proportion in ether and *spiritus conc.*; makes a cloudy mixture with equal volumes of carbon disulphide, benzene, and chloroform²⁾; sulphuric acid, ferric chloride and ammonia tests. Water shaken up with oil of cloves should not give an acid reaction³⁾.

¹⁾ Freshly distilled oil of cloves also gives a clearly perceptible, although very faint, acid reaction.

²⁾ The clouding is due to the water which occurs in the oil as a result of the process of manufacture; it disappears immediately upon the addition of a dehydrating agent, such as anhydrous sodium sulphate.

³⁾ Comp. Note 1.

Eucalyptus Oil (*Oleum Eucalypti*). From the leaves of *Eucalyptus Globulus* Labillardière. Colourless or very pale yellow; d_{15}° 0,850 to 0,866¹⁾; soluble in about 6 parts of *spiritus conc.*; boils at 170° and completely volatilises up to 200°.

¹⁾ In this respect, as in that of the solubility, the oil has been confounded with the distillate from *Eucalyptus amygdalina* Labill., which was official up to the present; (d_{15}° 0,850 to 0,886). The oil from *Eucalyptus Globulus* has a sp. gr. (at 15°) of 0,910 to 0,930, and is soluble in any proportion in *spiritus conc.* The indications of the Pharmacopœia in regard to the behaviour on boiling are also inaccurate.

Fennel Oil (*Oleum Foeniculi*). Colourless or faintly yellowish; d_{15}° 0,965 to 0,975; solidifies above 0°¹⁾; soluble in the equal vol. of *spiritus conc.*; ferric chloride test.

¹⁾ It must be borne in mind that in certain conditions fennel oil is capable of being cooled down considerably without solidifying; congelation must therefore be brought about if necessary by inoculation with a crystal of anethol. The congealing point of a good oil is not below +4°.

Juniper Oil (*Oleum Juniperi*). Colourless or greenish yellow; gives a neutral reaction; d_{15}° 0,60 to 0,70¹⁾; readily soluble in carbon

disulphide²), chloroform and benzene, less readily in *spiritus conc.* (1:10)³); resinifies on exposure to air.

¹) This statement is incorrect, and may possibly be due to an erratum the sp. gr. of juniper oil at 15° lies between 0,860 and 0,885.

²) Possible cloudiness is due to a slight percentage of water in the oil, the result of the process of manufacture; it disappears at once upon the addition of a dehydrating agent, such as anhydrous sodium sulphate.

³) Freshly distilled oils are soluble in 5 to 10 vols. of *spiritus conc.*, but the solubility decreases very rapidly.

Lavender Oil (*Oleum Lavandulæ*). Yellowish green or colourless¹); gives a neutral reaction²); $d_{15^{\circ}}$ 0,885 to 0,895; soluble in concentrated acetic acid³) and in 3 parts of 70 per cent. alcohol⁴).

¹) Frequently also pale yellow.

²) Almost all oils of lavender show a trace of free acid.

³) This test is quite useless.

⁴) Oils with a high percentage of ester often show opalescence, which usually persists even when more alcohol is added.

Lemon Oil (*Oleum Citri*). Pale yellow; $d_{15^{\circ}}$ 0,858 to 0,861¹); gives a clear solution with 5 parts of 96 per cent. alcohol.

¹) 0,857 would be a more correct value for the minimum.

Menthol (*Mentholum*). Colourless crystals; m. p. 42 to 43°¹); b. p. 212°²), almost insoluble in water, readily soluble in *spiritus conc.*, ether, and chloroform; 1 g. menthol should evaporate on the water-bath without leaving a residue; test for oily impurities.

¹) The m. p. lies between 43,5 and 44,5°.

²) Menthol boils at 217° if the mercury thread of the thermometer is wholly surrounded by the steam.

Mustard Oil (*Oleum Sinapis æthereum*). Colourless or yellowish; gives a neutral reaction; $d_{15^{\circ}}$ 1,016 to 1,025¹); boiling temperature 148 to 152°²); soluble in any proportion in ether and *spiritus conc.*, also in 10 parts of *spiritus dil.*; sulphuric acid and ferric chloride tests.

¹) The minimum limit should be 1,014.

²) This indication is not sufficiently explicit. The *greater part* of mustard oil boils between 148 and 153° if the mercury thread of the thermometer is wholly surrounded by the steam.

Neroli Oil (*Oleum Aurantii florum*). Faintly fluorescent; colourless¹) or pale yellow when freshly prepared, afterwards deep yellow; $d_{15^{\circ}}$ 0,870 to 0,880; soluble in 1 to 2 parts of *spiritus conc.*, turns cloudy when greatly diluted²).

¹) Neroli oil is never colourless, even freshly distilled oil is always yellowish.

²) The solubility referred to above applies to 80 per cent. alcohol.

Peppermint Oil (*Oleum Menthæ piperitæ*). Colourless or pale yellow; gives a neutral reaction¹); $d_{15^{\circ}}$ 0,900 to 0,910; gives a clear solution with an equal volume of *spiritus conc.* and 4 to 5 vols of *spiritus dil.*

¹) The oil almost always contains a trace of free acid.

Pine Needle Oil (*Oleum Pini silvestris*)¹). Colourless or faintly yellowish; $d_{15^{\circ}}$ 0,853 to 0,870; dissolves very readily in ether and in ten times its vol. of *spiritus conc.*

¹) *Oleum Pini silvestris* is an old but incorrect designation for oil from cones of *Abies alba*, which is, in fact, the oil intended here, as is evident from the sp. gr. mentioned. Genuine pine needle oil, *i. e.* the oil distilled from the needles of *Pinus silvestris* L. is not a commercial product at all. Comp. Report April 1909, 79.

Rose Oil (*Oleum Rosæ*). Viscous, yellowish, solidifies at 15 to 22°; $d_{15^{\circ}}$ 0,855 to 0,870¹); almost insoluble in water, soluble in 30 parts of *spiritus conc.* with opalescence²).

¹) As rose oil is still solid at 15° its sp. gr. should be taken above that temperature. At $\frac{30^{\circ}}{15^{\circ}}$ (as required, for instance, by the British Pharmacopœia) the limits of value, according to our experience, lie between 0,849 and 0,863.

²) The imperfect solubility in alcohol is due to the high paraffin content of the oil.

Terpin Hydrate (*Terpinum hydratum*). Colourless, lustrous, almost odourless crystals which, when heated rapidly, melt at 116°; soluble in about 250 parts of water, 10 parts of *spiritus conc.*, 100 parts of ether, and 200 parts of chloroform; the aqueous solution should not give an acid reaction; when heated with sulphuric acid an odour of terpineol appears; on a platinum sheet, terpin hydrate should burn up without leaving a residue.

Thymol (*Thymolum*). Colourless crystals; m. p. 50 to 51°; b. p. 228 to 230°¹); $d_{15^{\circ}}$ 1,028²); almost insoluble in water, readily soluble in *spiritus conc.*, ether, and chloroform, as well as in soda solution. When 1 g. of pulverised thymol is shaken up with 20 g. of water, the latter should not acquire an acid reaction or give a violet colour with ferric chloride. Heated upon the water bath, thymol must not leave a considerable residue.

¹) Thymol boils at 232° (753 mm.) when the entire mercury thread is surrounded by the steam.

²) The Pharmacopœia does not say how this difficult determination is to be carried out. It would have been sufficient to state that solid thymol sinks in water, while liquid thymol floats upon it.

Turpentine Oil, Rectified (*Oleum Terebinthinæ rectificatum*). Gives a neutral reaction; $d_{15^{\circ}}$ 0,860 to 0,870; boiling temperature 155 to 162°; soluble in 9 parts of *spiritus conc.*; resinifies when exposed to the air.

Italian Pharmacopœia.

(Farmacopea Ufficiale del Regno d'Italia, ed. III.)

The Italian Pharmacopœia which has been in force since 1904 has now been replaced by a new (the third) Edition, which we

propose to review here so far as the essential oils and allied products enumerated in it are concerned. The general impression produced upon scanning the several paragraphs is by no means overwhelmingly favourable; here and there the work even shows a certain superficiality, nor does it exhibit any very marked advance upon the often very faulty statements of the previous edition. It would have been very appropriate if the criticisms which have been passed upon its predecessor had been taken to heart in a greater measure in the compilation of the present Pharmacopœia. It must be admitted that, here and there, pains have been taken to introduce more scientific tests; in the case of certain oils, for instance, the method of quantitative determination of the principal constituents has been introduced, but on the other hand obsolete methods of examination, such as the iodine-test, have been retained. Similarly the statement, repeated in almost every instance, that a given oil is soluble with any proportion of absolute alcohol, is superfluous, because it signifies nothing that is characteristic of the particular oil. Attention has also been paid in many cases to the behaviour of the oil under boiling, but nothing is said as to the manner in which the process is to be carried out, although such indications would be of particular importance here. We have repeatedly dwelt upon this point in our criticisms of Pharmacopœias.¹⁾

None of the oils previously omitted have been struck out; on the other hand eucalyptus oil, lavender oil, and synthetic wintergreen oil have been newly incorporated; oil of Roman chamomile appears to be recognised in addition to ordinary oil of chamomile, — at any rate, its sp. gr. is stated, and under cinnamon oil the sp. gr. of cassia oil and of Ceylon cinnamon oil are mentioned.

We specify below the various oils and preparations thereof for particular notice: —

Anise Oil, Russian (*Essenza di anice*). Colourless or yellowish; $d_{20^{\circ}}$ 0,980 to 0,990; when cooled, congeals into a crystalline mass which begins to melt at 15° and liquefies again completely between 19° and 20° ¹⁾; sol. 1 vol. in 2 to 3 of 90 per cent. alcohol.

¹⁾ Congelation does not always occur spontaneously; in certain conditions it may be necessary to introduce a little solid anethol or solid anise oil into the cooled oil; an anise oil of good quality only begins to melt again at above 17° . If kept in half-filled bottles, as well as after repeated melting, anise oil loses its power of congelation more and more. Comp. Report October 1904, 42.

Cajeput Oil (*Essenza di cajeput*). Colourless, occasionally greenish owing to traces of copper; $d_{15^{\circ}}$ 0,920 to 0,930¹⁾; sol. in its own

¹⁾ Compare, for example, the present Report, p. 124; Report April 1908, 127. April 1909, 100.

vol. of 90 per cent. alcohol²⁾; when 1 cc. oil is shaken with 10 cc. dilute hydrochloric acid, the aqueous solution when separated out from the oil should not assume a reddish brown colour with ferrocyanide of potassium (copper test).

¹⁾ As the minimum limit 0,919 is more correct.

²⁾ Cajeput oil is soluble in any proportion with 90 per cent. alcohol.

Camphor (*Canfora*). A white, crystalline, translucent mass; d_{15}° 0,993¹⁾; m. p. 175°; burns with a luminous flame and volatilises at normal temperature; almost insoluble in water (1:1200), readily in alcohol, ether, chloroform, acetic acid, fixed and essential oils. 0,1 g. camphor should volatilise without leaving a residue; chlorine-test.

Natural camphor is optically active, synthetic camphor inactive

¹⁾ This statement serves no purpose, especially as nothing is said as to the manner in which the determination is to be carried out. The value given above is only approximate.

Cassia Oil, see Cinnamon Oil.

Chamomile Oil (*Essenza di camomilla comune*). Blue, turns brown¹⁾ when exposed to air or in contact with an alcoholic solution of caustic soda; d_{15}° 0,930 to 0,945²⁾; oil of Roman chamomile³⁾ has d_{15}° 0,905 to 0,915; sol. 1 vol. in 8 of 90 per cent. alcohol, occasionally with opalescence⁴⁾; when cooled down to 0° it becomes viscous but without congealing⁵⁾.

¹⁾ It turns green as an intermediate colour.

²⁾ The minimum limit should be reduced to 0,925.

³⁾ It would have been better to enumerate this oil separately, as it is altogether different from ordinary chamomile oil; in dealing with the other requirements of the Pharmacopœia we refer exclusively to the ordinary oil.

⁴⁾ Owing to its high paraffin content, chamomile oil only gives cloudy mixtures with 90 per cent. alcohol.

⁵⁾ This statement is not correct; at 0° chamomile oils forms a moderately solid mass.

Cinnamon Oil (Cassia Oil and Ceylon Cinnamon Oil) (*Essenza di cannella*). Colourless or pale yellow, turns yellow to brown with age¹⁾; sol. 1 vol. in 3 of 70 per cent. alcohol²⁾; d_{15}° of Ceylon cinnamon oil 1,024 to 1,040, d_{15}° of cassia oil 1,055 to 1,065³⁾; nitric acid and ferric chloride reactions; cinnamic aldehyde content not less than 70%⁴⁾.

¹⁾ Cassia oil is from the first deep yellow to brown; neither of the oils is colourless.

²⁾ In the case of cassia oil the solution is usually not quite clear.

³⁾ The maximum limit is too low; it should be 1,070.

⁴⁾ This is correct for neither oil. In the case of Ceylon cinnamon oil the aldehyde content ranges from 65 to 76%; while cassia oil should have at the very least 75%.

Citron Oil (Cedro Oil) (*Essenza di cedro*)¹⁾. Greenish-yellow; the oil obtained by steam distillation is colourless²⁾; d_{15}° 0,857 to 0,860³⁾;

very sparingly soluble in water, sol. 1 vol. in about 5 of 90 per cent. alcohol⁴) and in any proportion in absolute alcohol.

¹) From the sp. gr. demanded it is evident that *lemon oil* (*essenza di limone*) is meant here, inasmuch as the various citron or cedro oils, which for the rest are not commercial articles at all, are partly heavier and partly lighter than stated above. Comp. Bericht October 1895, 18; Report April 1902, 30; April 1903, 33.

²) Lemon Oil has a pale yellow colour. Oils obtained by distillation are of inferior value and do not keep at all.

³) The maximum limit is too high; it should be 0,861.

⁴) The solution, for which from 6 to 8 vols. of 90 per cent. alcohol are required is frequently rendered turbid by mucous or vegetable-wax-like constituents.

Clove Oil (*Essenza di garofani*). Yellowish, gradually turning brown on exposure to air; $d_{15^{\circ}}$ 1,045 to 1,070; sol. 1 vol. in 2 of 70 per cent. alcohol; eugenol content not less than 85% (determined with a 5% caustic soda solution¹); identity-reactions and test for phenol.

¹) Comp. Report April 1907, 118.

Eucalyptol (*Eucaliptolo*). Colourless; $d_{15^{\circ}}$ 0,930¹); b. p. 176 to 177°; congeals in a freezing mixture to a crystalline mass which again melts at — 1°²); identity tests with bromine; eucalyptol should give a clear solution with its own vol. of carbon disulphide (test for water).

¹) The sp. gr. lies between 0,928 and 0,930 (15°).

²) Eucalyptol melts at + 1 to + 1,5°. Congelation must be induced, if necessary by rubbing the side of the vessel with a glass rod.

Eucalyptus Oil (*Essenza di eucalipto, Globulus*). Pale yellow¹) $d_{15^{\circ}}$ 0,910 to 0,930; sol. 1 vol. in 3 of 70 per cent. alcohol. Eucalyptol content not less than 70% (resorcinol method)²).

¹) Eucalyptus oil is colourless, pale yellow, or pale green.

²) The Pharmacopœia here prescribes the determination originally recommended by us; by requiring the shaking of 10 cc. of oil with 90 cc. of 50 per cent. resorcinol solution. But as this method often gave excessively high results we modified it slightly afterwards. Comp. Report April 1908, 50.

Juniper Berry Oil (*Essenza di ginepro*). Colourless or pale greenish yellow; thickens under the influence of light and air and then acquires a more yellow colour; $d_{15^{\circ}}$ 0,865 to 0,885¹); sol. 1 vol. in 9 of 90 per cent. alcohol²) and in 1 part of carbon disulphide³).

¹) The minimum limit is too high, it should be 0,860.

²) Only freshly distilled oils meet with this requirement; the solubility decreases rapidly.

³) Possible clouding is ascribable to a low water content, due to the mode of preparing the oil.

Juniper Oil, Empyreumatic (Cade Oil) (*Olio cadino*)¹). Deep brown; $d_{15^{\circ}}$ 0,99 to 1,05; very sparingly soluble in water, soluble in ether, chloroform and absolute alcohol; with carbon disulphide and benzene it makes only cloudy mixtures; about 65% of the oil should pass over between 150 and 300°; identity-reactions.

¹) For cade oil and its properties comp. our Reports November 1908, 24 and April 1909, 58.

Lavender Oil (*Essenza di lavanda*). Colourless¹), pale yellow or pale green; $d_{15^{\circ}}$ 0,885 to 0,895; sol. 1 vol. in 3 of 70 per cent. alcohol; linalyl acetate content not less than 35⁰/₀; test for citric acid esters.

¹) Only rectified lavender oils are colourless, but these are of inferior value. Comp. Report October 1894, 32.

Menthol (*Mentolo*). Colourless prisms; m. p. 42 to 43⁰); b. p. 212⁰); almost insoluble in water, very readily in alcohol and ether; 0,1 g. menthol when evaporated in the water bath should leave no ponderable residue; test for thymol.

¹) The m. p. lies between 43,5 and 44,5⁰.

²) Menthol boils at 216⁰ (753 mm.) if the mercury thread of the thermometer is wholly surrounded by the steam.

Mustard Oil, artificial and natural (*Essenza di senape*). Colourless, afterwards yellowish with a reddish tinge; $d_{15^{\circ}}$ of the artificial oil 1,020, of the natural oil 1,018 to 1,025¹); b. p. 148⁰); readily soluble in alcohol, ether, and carbon disulphide, very sparingly in water (1 : 1000); identity-reactions; allyl isothiocyanate content 94 to 99⁰/₀ ³).

¹) The sp. gr. given here is inaccurate; in the case of artificial oil, it ranges from 1,020 to 1,025, in the natural oil from 1,014 to 1,025 (15⁰).

²) This also requires correction: mustard oil boils *principally* between 147 and 153⁰.

³) The Pharmacopœia gives detailed instructions for the carrying out of this determination, but gives inaccurate data of the consumption of ammonium sulphocyanide solution. According to these the oil should contain over 150⁰/₀ allyl isothiocyanate. We again refer here especially to the statements in our Reports with regard to the testing of mustard oil. Report April 1906, 45; April 1908, 69.

Neroli Oil (*Essenza di fiori d'arancio amaro*). Yellow, turns reddish under the influence of light and air; blue fluorescence; $d_{15^{\circ}}$ 0,870 to 0,880, sol. 1 vol. in 1 to 2 of 90 per cent. alcohol, on further dilution opalescence¹).

¹) This statement is correct for 80 per cent. alcohol; neroli oil gives a clear solution with any proportion of 90 per cent. alcohol, although after some time in this case also slight opalescence ensues owing to the separation of paraffin.

Peppermint Oil (*Essenza di menta*). Colourless, straw-coloured or greenish; gradually turns yellow and thickish when exposed to air; $d_{15^{\circ}}$ 0,890 to 0,920; $d_{15^{\circ}}$ of the Italian oil 0,908 to 0,925; English oil is soluble in 3 to 5 times its own vol. of 70 per cent. alcohol¹), Italian oil occasionally gives with 2 vols. a slightly opalescent solution which does not become clear on further dilution; congeals at — 8⁰ to — 20⁰, menthol being separated; Italian oil does not congeal at — 17⁰. Colour test with glacial acetic acid and nitric acid.

¹) American oil, which (judging by the sp. gr.) is also official, usually give a slightly opalescent solution; this is also sometimes the case with English oil.

Rosemary Oil (*Essenza di rosmarino*). Colourless or yellowish green; $d_{15^{\circ}}$ 0,90 to 0,92; sol. 1 vol. in 10 of 90 per cent. alcohol¹).

¹) Rosemary oil is soluble with one-half its vol. of 90 per cent. alcohol.

Sandalwood Oil (*Essenza di sandalo*). More or less yellow $d_{15^{\circ}}$ 0,975 to 0,985; sol. 1 vol. in 5 of 70 per cent. alcohol; santalol content ($C_{15}H_{24}O$) 77 to 84%¹⁾.

¹⁾ This is an inaccurate statement, nor does it agree with the Pharmacopœia requirements as to the mode of determination. The latter rather show that a santalol content of at least 90,27% is demanded.

Terpin Hydrate (*Terpina idrata*). Lustrous, colourless and odourless prisms. When dried *in vacuo* or over sulphuric acid it loses about 9,5% of water and is converted into terpin, which melts at 105 to 106°; sol. in about 250 parts of cold or 32 parts of boiling water; also in 10 parts of alcohol; insoluble in petroleum ether; the aqueous solution should be neutral; when an aqueous solution acidulated with sulphuric acid is boiled the odour of terpineol appears; 0,1 g. terpin hydrate should burn without leaving a residue.

Thymol (*Timolo*). Colourless, transparent crystals, m. p. 50 to 51°¹⁾; b. p. 228 to 230°²⁾; slightly soluble in water (about 1:1200), the aqueous solution should be neutral; soluble in less than its own vol. of alcohol, very readily in ether, glacial acetic acid and fixed oils; 0,05 g. thymol should volatilise completely on the water bath; identity reactions, test for phenol.

¹⁾ The m. p. lies between 50,5 and 51,5°.

²⁾ Thymol boils at 232° (753 mm.) if the mercury thread is wholly surrounded by the steam.

Turpentine Oil, rectified (*Essenza di trementina*). Colourless $d_{15^{\circ}}$ 0,865 to 0,875; boils between 155 and 162°; entirely volatile; almost insoluble in water, sol. 1 vol. in 12 of 90 per cent. alcohol; in any proportion in absolute alcohol, ether, chloroform, carbon disulphide, fixed and essential oils; resinifies when exposed to air; neutral reaction, when kept in a bottle only partly filled the oil turns yellow and acquires an acid reaction. The crude oil, which may be used for certain purposes, is colourless or pale yellow and leaves about 2% of residue on evaporation¹⁾.

Old, ozonised oil should also be in stock; this oil gives a yellow colour to starch-paste treated with iodide of potassium.

¹⁾ Comp. this Report, p. 116.

Wintergreen Oil, artificial (*Salicilato di metile*). Colourless; soluble in alcohol and ether, almost insoluble in water; $d_{15^{\circ}}$ 1,182 to 1,187¹⁾; b. p. 218 to 221°. Identity-reaction with ferric chloride.

¹⁾ These limits of value are incorrect; the sp. gr. ranges from 1,185 to 1,190 (15°).

Pharmacopœia of the United States.

Before the American Pharmaceutical Society, Jeancard and Satie¹⁾ have criticised the requirements of the U. S. Pharmacopœia with regard

¹⁾ Americ. Perfumer 4 (1910), 207.

to essential oils, and their paper has been published in *The American Perfumer*. The authors begin by reviewing the requirements of the Pharmacopœia with regard to specific gravity, rotation, solubility, saponification, etc., after which they criticise the description of the various oils and the tests prescribed for them.

Soon after the publication of the last Edition of the Pharmacopœia we published a detailed critical review of those parts of the work which deal with essential oils¹⁾, and there is consequently no reason for us to revert to the subject. We will therefore content ourselves with calling attention to the paper by Jeancard and Satie, referring at the same time to our previous statements.

Suggestions for the new British Pharmacopœia.

As long ago as the year 1906, the prospective publication of a new Edition of the British Pharmacopœia caused the Commission charged with the compilation of that work to make, and submit to public discussion, suggestions for improvements in the description and testing of the various articles. The suggestions included short references to certain essential oils, to which we referred at the time²⁾. Hill and Umney³⁾ have now, in a very thorough manner, taken up the question of the requirements to which the official essential oils should be made to meet, bringing forward general points of view as well as discussing the various oils separately. It should be stated at the outset that the object of Hill and Umney's publication is to take the greatest possible advantage of the progress which has been made in the testing of essential oils, in order to enable pharmacists in all cases to form a serviceable judgment of the value and purity of the oils. If, therefore, in the subjoined paragraphs we again enter into details, our reason for doing so is that on many points our opinion differs from that of Hill and Umney, and because we regard it as useful to express our views on the subject.

We will preface our criticisms by pointing out that as regards the determination of the boiling point it is necessary to give very detailed particulars with regard to the form of the flask to be employed, the speed at which the distillation takes place, and the manner in which the thermometer is to be introduced. The latter should be placed in such a way that the degree indicating the b. p. is a little above the delivery-tube, so that the entire mercury-thread is washed by the steam from the liquid. It goes without saying that the mercury-bulb should not project into the hollow of the flask, or even into the liquid. All these details

¹⁾ Report October 1905, 73; April 1906, 69; October 1907, 101.

²⁾ Report April 1907, 107.

³⁾ Chemist and Druggist 76 (1910), 271.

are of the greatest importance. Up to the present all cases in which we have received complaints on account of an alleged incorrect boiling-point have, upon investigation, been found to be due to some mistake in making the test. For this reason we would also recommend that statements relating to the b. p. should be omitted in all cases in which better means are available for estimating the quality of an oil, as, for instance, in the case of oils of anise and caraway.

Hill and Umney also refer to the refractive index of the majority of the oils. But as this constant is precisely the one which is almost invariably the least characteristic of the particular oil concerned, and as the limits of value have as yet by no means been laid down with sufficient accuracy, we regard the inclusion of the refractive index of oils into a Pharmacopœia as wholly unsuitable, or at any rate as premature. For this reason we have left this constant out of account altogether.

In what follows the suggestions made by Hill and Umney are given first, in order to make it easier to follow our footnotes.

Anise Oil and Star Anise Oil (*Oleum Anisi*). $d_{20^{\circ}}$ 0,975 to 0,990, rising on keeping; α_D to the left, up to $-2^{\circ 1}$; congeals when stirred at about $+10^{\circ}$, and should not melt again below $+15^{\circ 2}$; at least 80% should distil between 225 and 235 $^{\circ 3}$; sol. 1 vol. in 3 of 90% alcohol.

¹⁾ Star anise oil is sometimes faintly dextrorotatory.

²⁾ We recommend that the congealing point be determined *lege artis*, and that $+15^{\circ}$ be required as the minimum; the oil should at the same time be cooled to 10° and should then be inoculated with a little solid anethol.

³⁾ With regard to b. p. determinations see introduction to this article. In the case of oil of anise we regard the congealing point as a far better measure of value.

Cajuput Oil (*Oleum Cajuputi*). $d_{15,5^{\circ}}$ 0,919 to 0,930; α_D lævorotatory, not more than $-2^{\circ 1}$; cineolcontent, determined by the phosphoric acid method, at least 45 per cent. by vol.²⁾

¹⁾ We have met with genuine samples with rotations up to $-3^{\circ}40'$.

²⁾ We cannot understand how Hill and Umney can recommend so unreliable a method as the determination of cineol by means of phosphoric acid for incorporation into the Pharmacopœia. They appear never to have carried out determinations with mixtures of known cineol content, otherwise they would have come to a different conclusion. Also comp. our Reports April 1906, 72; October 1907, 48; April 1908, 50.

Caraway Oil (*Oleum Carui*). $d_{15,5^{\circ}}$ 0,910 to 0,920; $\alpha_D +75$ to $+82^{\circ 2}$; soluble in equal vol. of 90 per cent. and in 10 volumes of 60 per cent. alcohol³⁾. When distilled from a Wurtz flask at the rate of 1 drop per second at least 50% should distil above 200 $^{\circ 4}$.

¹⁾ We should regard 0,908 as a more appropriate minimum limit.

²⁾ The minimum limit is too low; it should be $+70^{\circ}$.

³⁾ Here 60 per cent. alcohol is an error for 80 per cent. alcohol.

⁴⁾ This test is intended to show the carvone content. It would, however, be more correct to substitute for it the direct determination of carvone by means of neutral sulphite. The carvone content varies from 50 to 60%.

Cinnamon Oil, Ceylon (*Oleum Cinnamomi*). $d_{15,5^{\circ}}$ 1,025 to 1,040¹⁾; α_D — 0°30' to — 1°; soluble 1 vol. in 3 to 4 of 70 per cent. alcohol; ferric chloride test; cinnamic aldehyde content 55 to 75 % (determined with neutral sulphite)²⁾.

¹⁾ The minimum limit is too high; it should be 1,023.

²⁾ We have found the aldehyde content of normal oils distilled by ourselves from Ceylon cinnamon to vary from 65 to 76 %. Oils with an aldehyde content of from 55 to 65 % are, to say the least, suspect.

Clove Oil (*Oleum Caryophylli*). $d_{15,5^{\circ}}$ 1,047 to 1,070; soluble 1 vol. in 3 of 70 per cent. alcohol; ferric chloride test; eugenol content at least 80 per cent. by volume¹⁾.

¹⁾ Hill and Umney carry out this test with a 5 per cent. solution, it is preferable to use a 3 per cent. solution. Comp. Report April 1907, 118.

Copaiba Balsam Oil (*Oleum Copaibæ*). $d_{15,5^{\circ}}$ 0,900 to 0,910¹⁾; α_D — 7 to — 35°²⁾; distils between 250 and 275°³⁾. Colour-test with nitric acid for the detection of gurjun oil⁴⁾.

¹⁾ We have found the sp. gr. of good oils to run as high as 0,925.

²⁾ The rotation is frequently rather lower.

³⁾ With regard to the determination of the boiling point see the introductory paragraph.

⁴⁾ We regard such tests as affording no proof.

Coriander Oil (*Oleum Coriandri*). $d_{15,5^{\circ}}$ 0,870 to 0,885; α_D + 8 to + 14°; soluble 1 vol. in 3 of 70 per cent. alcohol.

Cubeb Oil (*Oleum Cubebæ*). $d_{15,5^{\circ}}$ 0,910 to 0,930; α_D — 25 to — 40°; at least 80 % of the oil should distil between 250 and 280°¹⁾.

¹⁾ With regard boiling temperature see the introductory paragraph.

Dill Oil (*Oleum Anethi*). Pale yellow, darkening on keeping; $d_{15,5^{\circ}}$ 0,900 to 0,910¹⁾; α_D + 70 to + 75°²⁾; soluble 1 vol. in 3 of 90 per cent. alcohol.

¹⁾ The maximum limit is too low; it should be 0,915.

²⁾ We have found our own distillates to show an opt. rot. of up to 80°.

We should recommend the quantitative determination of carvone with neutral sulphite. We have found it to range from 48 to 59 % in oils distilled by ourselves, and occasionally as low as 40 % in the case of commercial oils.

Eucalyptus Oil (*Oleum Eucalypti*). $d_{15,5^{\circ}}$ 0,910 to 0,930; α_D + 10 to — 10°; soluble 1 vol. in 5 of 70 per cent. alcohol; cineol content, determined by the phosphoric acid method, at least 55 per cent. by volume¹⁾; the oil should give no phellandrene-reaction.

¹⁾ Comp. note 2 under Cajuput oil.

Juniper Oil (*Oleum Juniperi*). $d_{15,5^{\circ}}$ 0,862 to 0,890¹⁾; increasing with age; α_D — 3 to — 12°²⁾; soluble, when freshly distilled, 1 vol. in 4 of 95 per cent. alcohol, becoming less soluble with age³⁾.

¹⁾ The minimum limit is too low; it should be 0,860.

²⁾ The following values would be more in accordance with facts, viz., α_D to the left up to — 15°.

³⁾ Freshly distilled oils are soluble 1 vol. in 5 to 10 of 90 per cent. alcohol.

Lavender Oil (*Oleum Lavandulæ*). $d_{15,5^{\circ}}$ 0,883 to 0,900; α_D — to -10° ; soluble 1 vol. in 3 of 70 per cent. alcohol¹); estercontent of English oil 7 to 11⁰/₀, of French not less than 30⁰/₀.

¹) Oil, with a high ester content (40⁰/₀ and over) are sometimes less soluble

Lemon Oil (*Oleum Limonis*). $d_{15,5^{\circ}}$ 0,857 to 0,860¹); $\alpha_{D20^{\circ}}$ $+5$ to $+64^{\circ}$; citralcontent at least 3,5⁰/₀.

¹) We should regard 0,861 as the more correct maximum value.

²) Hill and Umney state that the merits of the various processes for the determination of citral in lemon oil are at present under investigation. The incorporation into the Pharmacopœia of a citraldetermination would be premature in the case of lemon oil, inasmuch as none of the methods suggested up to the present have been proved to be reliable. Moreover, adulteration of lemon oil is least likely to be detected by this method. Notwithstanding the opposite opinion of Mr. Umney (see p. 66), we regard our distilling-method as much more useful for this purpose. The difference between the rotation of the original oil and the first 10⁰/₀ of the distillate should not exceed a maximum of 5⁰ (according to Chace, see p. 65, 6⁰) provided our method be followed exactly. (Report October 1898, 41.)

Mustard Oil (*Oleum Sinapis*). $d_{15,5^{\circ}}$ 1,018 to 1,023¹); distilled between 148 and 156⁰, allyl isothiocyanate at least 92⁰/₀²).

¹) These values are incorrect; the sp. gr. of natural mustard oil at 15⁰ varies from 1,014 to 1,025.

²) Hill and Umney give at the same time a method for determining the content. Their minimum requirement of deci-normal silver nitrate solution for 0,1 g. of oil however, corresponds to a content of 93,2⁰/₀ allyl isothiocyanate. We regard the value of 92⁰/₀ mentioned above as more appropriate. For the method to be followed in the determination we refer to our Reports of April 1906, 45 and April 1908, 70.

Nutmeg Oil (*Oleum Myristicæ*). $d_{15,5^{\circ}}$ 0,870 to 0,920¹); α_D $+1$ to $+30^{\circ}$ ²); soluble 1 vol. in 3 of 90 per cent. alcohol, test for fixed nutmeg oil.

¹) The maximum limit is too low; it should be 0,930.

²) Oils of our own distilling, from the best material, have given rotations as low as $+7^{\circ}52'$. Comp. Report October 1904, 65.

Peppermint Oil (*Oleum Menthæ piperitæ*). $d_{15,5^{\circ}}$ 0,900 to 0,920 α_D — 20 to — 35⁰¹); sol. 1 vol. in 4 of 70 per cent. alcohol²); menthyl acetate content at least 6⁰/₀³), menthol, free and combined, at least 50⁰/₀.

¹) As the values relating to sp. gr. also include American oil, this fact should be considered in the rotation, of which the minimum limit of value should be placed at — 18⁰.

²) Peppermint oil is soluble 1 vol. in 3 to 5 of 70 per cent. alcohol. When more alcohol is added, opalescence frequently ensues, especially in the case of American oil.

³) According to our observations the estercontent of the best oils varies from 3,5 to 18⁰/₀; the values given above should therefore be reduced.

Pimento Oil (*Oleum Pimentæ*). $d_{15,5^{\circ}}$ 1,040 to 1,055¹); α_D to the left, up to — 4⁰²); sol. 1 vol. in 3 of 70 per cent. alcohol; eugenol content not less than 65 per cent. by vol.³)

¹) The minimum limit is too high; it should be 1,024; comp. Bericht April 1899, 39.

²⁾ The rotation may go to -5° .

³⁾ For this test a 5 per cent solution is prescribed, which, however, gives much too high results with pimento oil. For this reason we recommended some years ago the use of a 3 per cent. solution. Comp. Report April 1907, 119.

Pine Needle Oil (*Oleum Pini*). Hill and Umney suggest that the place of this oil should be taken in the Pharmacopœia by oil distilled from the fresh leaves of the *Siberian pine*, (see below) which is readily procurable and has an equal medicinal value and a more agreeable odour. As to this, opinions may differ.

Roman Chamomile Oil (*Oleum Anthemidis*). $d_{15,5^{\circ}}$ 0,905 to 0,915; $\alpha_D + 1$ to $3^{\circ 1)}$; sol. in less than its own volume of 90 per cent. alcohol.

¹⁾ The rotation is frequently less than $+1^{\circ}$; comp. Report April 1909, 31. The determination of the sap. no. (which lies between 250 and 317) is also to be recommended.

Rose Oil (*Oleum Rosæ*). $d_{15,5^{\circ}}^{30^{\circ}}$ 0,855 to 0,862 ¹⁾; $\alpha_D - 2$ to $-4^{\circ 2)}$; m. p. 20 to 22,5 ³⁾.

¹⁾ The minimum limit is too high; it should be 0,849.

²⁾ According to our observations the rotation ranges from $-1^{\circ}30'$ to 3° .

³⁾ We should regard it as more correct to follow the general usage and give not the m. p., but the congealing point of rose oil. This lies between $+19$ and $+23,5^{\circ}$.

It would be of importance, in the case of rose oil, to ascertain the content of totalgeraniol, which is from 66 to 75 %₀. For pharmacists, however, this test would be somewhat expensive.

Rosemary Oil (*Oleum Rosmarini*). $d_{15,5^{\circ}}$ 0,900 to 0,920; α_D to the right up to $+15^{\circ}$; sol. 1 vol. in 5 to 10 of 80 per cent. ¹⁾ and in its own vol. of 90 per cent. alcohol; bornyl acetate content not less than 2 %₀ ²⁾; borneol content not less than 10 %₀.

¹⁾ French rosemary oil sometimes gives slightly cloudy solutions with 80 per cent. alcohol.

²⁾ This value should be reduced to 1 %₀.

Sandalwood Oil (*Oleum Santali*). $d_{15,5^{\circ}}$ 0,973 to 0,985; $\alpha_D - 16$ to $-20^{\circ 1)}$; sol. 1 vol. in 6 of 70 per cent. alcohol (at 20°); content of total santalol ($C_{15}H_{24}O$) not less than 90 %₀.

¹⁾ We recommend -21° as the maximum limit.

Spearmint Oil (*Oleum Menthæ viridis*). $d_{15,5^{\circ}}$ 0,925 to 0,940 ¹⁾; $\alpha_D - 30$ to $-50^{\circ 2)}$; sol. with an equal vol. of 80 per cent. alcohol ²⁾, the solution becoming turbid on further dilution. Sol. 1 vol. in 3 of 90 per cent. alcohol ³⁾.

¹⁾ The minimum limit is too high; it should be 0,920.

²⁾ Sol. up to 1 vol. in $1\frac{1}{2}$ of 90 per cent. alcohol.

³⁾ With 90 per cent, alcohol, spearmint oil at first gives a solution in any proportion; but in this case also opalescence or turbidity ensues on further dilution.

The carvone content of spearmint oil is from 40 to 50 %₀, in some cases even higher.

Turpentine Oil, Rectified (*Oleum Terebinthinæ rectificatum*). $d_{15,5^\circ}$ 0,860 to 0,870; distils almost entirely between 160 and 180°¹⁾ without leaving any considerable residue.

¹⁾ Rectified turpentine oil distils chiefly between 155 and 165°.

Oils which should be officially recognised.

Fennel Oil (*Oleum Fœniculi*). $d_{15,5^\circ}$ 0,960 to 0,990¹⁾; $\alpha_D + 6$ to $+ 20^\circ$ ²⁾; m. p. not less than $+ 4^\circ$ ³⁾; soluble with an equal vol. of 90 per cent. alcohol.

¹⁾ The limits may be drawn closer, at 15° the values lie between 0,965 and 0,977.

²⁾ These data are inaccurate; the rotation ranges between $+ 11$ and $+ 24^\circ$.

³⁾ It is desirable to demand that the congealing-point shall not be below $+ 4^\circ$. In order to ascertain this point the oil should be cooled down to about 2 to 3° and a little solid anethol introduced into it.

Orange Oil (*Oleum Aurantii*). $d_{15,5^\circ}$ 0,847 to 0,853¹⁾; $\alpha_D 20^\circ + 92$ to $+ 98^\circ$ ²⁾.

¹⁾ The limits given directly exclude oil of bitter orange, notwithstanding that Hill and Umney desire to admit both the bitter and the sweet oils into the Pharmacopœia. The requirements, correctly stated, should be: d_{15° 0,848 to 0,857.

²⁾ The lower limit is inexact; it should be $+ 90^\circ$. In this case also we recommend, exactly as in that of lemon oil, that the first 10% be distilled off according to the method indicated by us, and the rotation of the distillate ascertained. It should be not, or only slightly, less than the rotation of the original oil.

Pine Needle Oil, Siberian (*Oleum Pini*). $d_{15,5^\circ}$ 0,900 to 0,920¹⁾; $\alpha_D - 32$ to $- 42^\circ$ ²⁾; ester content (calculated as bornyl acetate) 30 to 40%³⁾.

¹⁾ The sp. gr. at 15° ranges from 0,905 to 0,924.

²⁾ The rotation varies from $- 37$ to $- 43^\circ$.

³⁾ The minimum limit is 29%.

Thyme Oil (*Oleum Thymi*). $d_{15,5^\circ}$ 0,920 to 0,950¹⁾; α_D faintly to the left; sol. 1 vol. in 2 of 80 per cent. alcohol. Phenol content not less than 25% by volume.

¹⁾ The minimum limit should be placed at 0,900, else it is out of harmony with the minimum phenol content allowed.

Wintergreen Oil (*Oleum Gaultheriæ* and *Oleum Betulæ*). Colourless¹⁾; $d_{15,5^\circ}$ 1,180 to 1,187²⁾; α_D 0 to $- 1^\circ$; sol. at 25°, 1 vol. in 6 of 70 per cent. alcohol³⁾; methylsalicylate content not less than 99%⁴⁾.

¹⁾ The oils generally have a reddish colour, due to traces of iron.

²⁾ The maximum limit should be raised to 1,188.

³⁾ Wintergreen oil dissolves 1 vol. in 5 to 7 of 70 per cent. alcohol.

⁴⁾ This requirement should be reduced to 98%.

In connection with the foregoing we desire to comment briefly upon certain criticisms to which the suggestions of Hill and Umney have been subjected in other quarters.

J. and G. Miller¹⁾ would regard it as very desirable if in the proposed new Pharmacopœia the necessary data were incorporated to admit of the detection of adulterations; according to them the factors laid down by Hill and Umney are insufficient for this purpose.

W. H. Simmons²⁾ generally agrees with the suggestions made by Hill and Umney, but offers the following observations thereon: —

Caraway Oil. The suggested distillation process to be replaced by the determination of the carvone content.

Clove Oil. A minimum content of 80% of eugenol.

The results obtained by us with our own distillates do not bear out the justice of this suggestion, for they show that the eugenol content of cloves very frequently falls below 85%. We should not regard it as proper to increase the percentage from 80 to 85.

Cinnamon Oil. It is recommended to fix a maximum limit for phenols (or eugenol) as determined by absorption with 5% caustic solution.

Coriander Oil. Determination of the percentage of alcoholic constituents by acetylation.

This we consider to be useless because in this case the alcohol occurs as linalool, which cannot be acetylated quantitatively.

Lavender Oil. The minimum limit of 30% for esters is too high, for some of the finest oils contain only 23 to 25% of linalyl acetate.

It is remarkable that, in spite of all our efforts, we have never yet met with such oils. All oils showing so low an ester content which we have examined have proved to be adulterated. We therefore regard the demand for a minimum of 30% of linalyl acetate as thoroughly justified.

Rose Oil. The minimum sp. gr. should be fixed at 0,850 ($\frac{30^\circ}{15^\circ}$). We suggest 0,849. See above.

Thyme Oil. For estimation of phenols a 10% caustic solution is recommended.

Our experience shows that this would be of no advantage; a 5 per cent. solution being sufficient.

With respect to general determinations, Simmons suggests that in the saponification process the boiling should be continued for half an hour only, instead of one hour. We cannot associate ourselves with this suggestion, as half an hour is not always long enough.

In the acetylation process Simmons recommends a preliminary saponification, but this we consider superfluous, because when the

¹⁾ Chemist and Druggist 76 (1910), 304.

²⁾ Ibidem.

original non-saponified oil is used, the determination is sufficiently exact for Pharmacopœia purposes. If it is desired to determine the alcohol content with exactness, and having regard to the estercontent, the proportion of free alcohol present can be ascertained from the difference between the ester-numbers of the original and the acetylated oil, and to this the proportion of esterified alcohol, as shown by the ester number, should be added. The total represents the percentage of total alcohols in the oil.

Evans Sons Lescher and Webb Ltd.¹⁾ offer remarks on the following oils: —

Anise Oil. Minimum limit for sp. gr. 0,978.

In the case of star anise oil we have met with a value as low as 0,975 (20°).

Cajuput Oil. $d_{15,5^{\circ}}$ 0,918 to 0,925.

Cinnamon Oil. $d_{15,5^{\circ}}$ 1,020 to 1,035¹⁾; aldehyde content 50 to 70%²⁾.

¹⁾ We have found oils distilled by ourselves to possess a sp. gr. of $d_{15^{\circ}}$ 1,023 to 1,040.

²⁾ Such a requirement would be quite wrong. Comp. our note on p. 135.

Clove Oil. The maximum limit of sp. gr. should be 1,065, besides which the phenol content should not be less than 85%¹⁾.

¹⁾ Comp. our note on p. 139.

Copaiba Balsam Oil. $d_{15,5^{\circ}}$ 0,898 to 0,910; α_D — 10 to — 35°¹⁾.

¹⁾ We fail to see any reason for departing from the present minimum limit of — 7°. We have met with oils of normal quality with an even lower opt. rot.

Coriander Oil. $d_{15,5^{\circ}}$ 0,870 to 0,880.

Cubeb Oil. $d_{15,5^{\circ}}$ 0,915 to 0,930.

Dill Oil. $d_{15,5^{\circ}}$ 0,902 to 0,915.

We should not recommend an increase in the minimum limit from 0,900 to 0,902, because such a suggestion would be in contradiction to our experience with pure distillates.

Lavender Oil. Evans Sons Lescher & Webb Ltd. have known good oils with an ester content as low as 28%¹⁾.

Orange Oil. $d_{15,5^{\circ}}$ 0,847 to 0,854¹⁾; α_D + 92 to + 99°²⁾.

¹⁾ Comp. our note on this subject, p. 138.

²⁾ Comp. our note on p. 138.

Pimento Oil. The sp. gr. never exceeds 1,050.

Rose Oil. $d_{15^{\circ}}^{30^{\circ}}$ 0,853 to 0,862¹⁾.

¹⁾ Comp. our note on p. 137.

¹⁾ Chemist and Druggist 76 (1910), 341.

Sandalwood Oil. The lowest rotation observed was -14° ; the santalol content of genuine oils is not less than 92% ¹⁾; a temperature of 21° is often required to yield a clear solution in 6 vols. of 70 per cent. alcohol.

¹⁾ We have repeatedly distilled oils from the best material which contained less than 92% of total santalol ($C_{15}H_{24}O$), and we can therefore see no ground whatever for raising the minimum limit from 90 to 92% .

W. Naumann¹⁾ pleads that no excessive importance shall be attached to physical constants. He thinks that careful indications as to the botanical origin and the odour of the oil are the main thing.

We are of opinion that it is impossible to dispense with fixed limits of value, which are applicable in all cases, for the sense of smell is only too often an untrustworthy guide as to the purity of an essential oil, although obviously the oil should satisfy all requirements in respect of its odour. But in our view, to regard the physical constants as a subsidiary criterion would be a retrograde step.

Going into particulars Naumann mentions: —

Eucalyptus Oil. The minimum cineol content required should be 70% .

Lavender Oil. The ester content of the best oils may be as low as 22% .

See our note on p. 139.

Peppermint Oil. If a solubility of 1:4 vols. of 70 per cent. alcohol is required it will probably often be necessary to redistil American oils.

Rose Oil. In the seasons 1905 and 1906 the sp. gr. of the finest oils was 0,853 to 0,854.

Rosemary Oil. Minimum limits of sp. gr. of 0,895 and 0,897 should be allowed.

We should not be in favour of reducing the minimum so much.

The Essential Oils dealt with on the Second International Congress of the White Cross.

Last October the second International Congress of the "White Cross" Association for Suppressing the Adulteration of Food-stuffs, Chemical Products and Drugs was held in Paris. In the course of the debates there was a discussion on essential oils, and resolutions were passed,

¹⁾ Chemist and Druggist 76 (1910), 341.

the publication of which calls for some comment here. Certain definite requirements were laid down for a whole series of the most commonly used essential oils, with the object of enabling consumers to satisfy themselves of their genuineness and purity. The basis of the requirements was formed by proposals formulated by a French committee, of which a copy was sent to us at the time, together with an invitation to visit the meeting. We dealt with the proposals in a detailed criticism, which was presented to the Congress, and we are glad to be able to state that by far the greater part of the suggestions made by us have been adopted in the Resolutions which were agreed to by the meeting and which have now been published. In reproducing the subjoined details representing the requirements with which, in the opinion of the meeting, the various oils should be made to conform, we are therefore able to restrict ourselves, with few exceptions, to observations intended to complete the demands of the meeting.

Almond Oil, Bitter. When freshly distilled colourless and neutral, becoming yellow and acquiring an acid reaction with age. d_{15° of oil containing hydrocyanic acid, 1,045 to 1,070; of oil free from hydrocyanic acid, 1,050 to 1,065¹⁾; $\alpha_D \pm 0^\circ$; sol. 1 vol. in 2 to 3 of 60 per cent., 1 vol. in 1 $\frac{1}{2}$ to 2 $\frac{1}{2}$ of 65 per cent. and 1 vol. in 1 to 2 of 70 per cent. alcohol. Should give no chlorine reaction.

¹⁾ The maximum limit of value for the sp. gr. of oil free from hydrocyanic acid is too high; it should be 1,055.

Anethol.¹⁾ d_{25° 0,984 to 0,986; $\alpha_D \pm 0^\circ$; sol. p. 21 to 22 $^\circ$; m. p. 22 to 23 $^\circ$.

¹⁾ Estragon oil is also, but incorrectly, included among oils containing anethol. Comp. Gildemeister and Hoffmann, *The Volatile Oils*, p. 44; Report November 1908, 66.

Anise Oil, Russian. Colourless; d_{20° 0,980 to 0,990; α_D not to the right; sol. p. +15 to +19 $^\circ$; anethol content 80 to 90 $\%$.

Bergamot Oil. More or less intense greenish-yellow¹⁾; d_{15° 0,880 to 0,887; α_D +8 to 25 $^\circ$; ester content (linalyl acetate) 30 to 45 $\%$; residue of evaporation 3 to 6 $\%$.

¹⁾ The colour varies from honey like to green.

In a Supplement the statement is made that pure oils, especially at the beginning of the season, sometimes contain less than 30 $\%$ of ester. It is also recommended to test for the addition of artificial esters.

Caraway Oil. Colourless, turns yellow with age; d_{15° 0,903 to 0,918; α_D +70 to +85 $^\circ$; carvone content 45 to 60 $\%$.

Cassia Oil. d_{15° 1,053 to 1,070, almost inactive¹⁾; aldehyde content 70 to 90 $\%$ ²⁾.

¹⁾ The rotation ranges from -1° to +6 $^\circ$.

²⁾ The minimum content should be 75 $\%$.

Cinnamon Oil, Ceylon. d_{15° 1,010 to 1,040¹⁾; α_D faintly lævotatory; aldehyde content 59 to 80%²⁾; phenol content 4 to 12%; sol. 1 vol. in 2½ of 80 per cent. alcohol³⁾.

¹⁾ The minimum limit should be 1,023.

²⁾ The cinnamic aldehyde content of Ceylon cinnamon oil is 65 to 76%. A higher content would point to the addition of cassia oil or of cinnamic aldehyde.

³⁾ Ceylon cinnamon oil is soluble in 2 to 3 vol. of 70 per cent. alcohol.

Clove Oil. When freshly distilled colourless or yellowish, afterwards brownish; d_{15° 1,040 to 1,068; eugenol content 70 to 92%.

Coriander Oil. d_{15° 0,870 to 0,885; α_D + 5 to + 13°¹⁾.

¹⁾ We have never known pure oils to rotate below + 8°.

Cumin Oil. d_{15° 0,900 to 0,930; α_D + 4 to + 8°; cuminic aldehyde content 30 to 50%¹⁾.

¹⁾ There is as yet no suitable method for determining the cuminic aldehyde content.

Cypress Oil. d_{15° 0,866 to 0,890; α_D + 4 to + 30°¹⁾.

¹⁾ The highest value observed by us is + 31°.

Eucalyptus Oil. d_{15° 0,910 to 0,930; α_D to the right, up to + 15°; eucalyptol content 55 to 80%¹⁾.

¹⁾ Sometimes the eucalyptol content is a little higher.

Fennel Oil. d_{15° 0,965 to 0,985¹⁾; α_D + 12 to + 24°. Sol. p. + 4 to + 6°²⁾.

¹⁾ We have never known fennel oil to exceed 0,977.

²⁾ Congelation may suitably be induced by introducing a little solid anethol, as the temperature of fennel oil, under certain conditions, can be lowered considerably without causing congelation. If the congealing point exceeds 6°, this, of course, affords no ground for rejection; it would in fact only indicate the genuineness of the oil.

Juniper Oil. d_{15° 0,860 to 0,885; α_D to the left, up to — 15°.

Lavender Oil. d_{15° 0,822¹⁾ to 0,895; α_D — 3 to — 9°; ester content (linalyl acetate) 28 to 60%²⁾; when testing, the addition of artificial esters should be looked for.

¹⁾ This is probably an erratum; it should be 0,882.

²⁾ It is expressly stated that unadulterated oils occur which contain as little as 25% of ester. This is contrary to our own experience; we should rather say that it is advisable to suspect all oils of which the estercontent falls below 30%.

Lemon Oil. d_{15° 0,857 to 0,862; α_{D20° + 57 to + 65°; residue of evaporation 2 to 5%; sol. 1 vol. in 0,3 to 5 of 95 per cent. alcohol.

Lemongrass Oil. d_{15° 0,870 to 0,913; citral content 60 to 87%¹⁾.

¹⁾ Both Malabar oil and so-called "West Indian" lemongrass oil meet these requirements.

Mandarin Oil. d_{15° 0,850 to 0,858¹⁾; α_D + 65 to + 75°.

¹⁾ The sp. gr. ranges from 0,854 to 0,859.

Mustard Oil. d_{15° 1,016 to 1,030¹⁾; sol. 1 vol. in 8 of 70 per cent. alcohol.

¹⁾ We have met with good quality oils with a sp. gr. of as low as 1,014.

Neroli Oil. $d_{15^{\circ}}$ 0,870 to 0,880; $\alpha_D + 1$ to $+ 6^{\circ 1)}$; sap. no. 20 to 52²⁾.

¹⁾ We have met with genuine samples which showed up to $+ 8^{\circ}$.

²⁾ In the course of the last few years we have met with pure oils of which the sap. no. was as high as 55.

Orange Oil, bitter. $d_{15^{\circ}}$ 0,848 to 0,854; $\alpha_{D20^{\circ}}$ $+ 92$ to $+ 98^{\circ 1)}$

¹⁾ Neither the values given above for the rotation nor those relating to the sp. gr. are in accord with the facts. The limits of value are as follows: $d_{15^{\circ}}$ 0,853 to 0,857, $\alpha_{D20^{\circ}}$ $+ 90$ to $+ 93^{\circ}$.

Orange Oil, sweet. $d_{15^{\circ}}$ 0,846¹⁾ to 0,853; $\alpha_{D20^{\circ}}$ $+ 95$ to $+ 99^{\circ}$.

¹⁾ We have never found the sp. gr. to fall below 0,848.

Peppermint Oil.

1. English. $d_{15^{\circ}}$ 0,900 to 0,910; $\alpha_D - 22$ to $- 33^{\circ}$; total menthol 55 to 66%, free menthol 50 to 60%, esterified menthol 5 to 16%.

2. American. $d_{15^{\circ}}$ 0,900 to 0,920; $\alpha_D - 25$ to $- 33^{\circ}$; total-menthol 50 to 64%, free menthol 40 to 55%, esterified menthol 10 to 24%.

3. French. $d_{15^{\circ}}$ 0,910 to 0,926; $\alpha_D - 6$ to $- 16^{\circ 2)}$; total-menthol 45 to 58%, free menthol 40 to 52%, esterified menthol 5 to 10%.

4. Japanese, dementholised. $d_{15^{\circ}}$ 0,894 to 0,900³⁾; $\alpha_D - 25$ to $- 35^{\circ}$; total menthol 45 to 70%, free menthol 40 to 65%, esterified menthol 3 to 13%⁴⁾.

¹⁾ The minimum limit is incorrect; it should be reduced to $- 18^{\circ}$.

²⁾ We have met with French oil down to $- 35^{\circ} 18'$. Comp. Report April 1905, 62.

³⁾ The sp. gr. of the oils of commerce ranges up to 0,905.

⁴⁾ As we informed the Committee at the time, we regard the giving of separate values for total menthol, free menthol and esterified menthol as quite unnecessary, and as needlessly complicating the examination. In our view it would be sufficient to indicate the content of total menthol, *i. e.* the value shown by the sap. no. of acetylated oil. It is true that by doing this the portion of menthol which occurs in the oil in the esterified state is disregarded, but the values obtained can only be too high to the extent of about 3%, and are therefore quite accurate enough for practical purposes. If it is desired to determine the content of total menthol taking into account the ester content, this can be done by the method described on p. 139. Our own experience of the menthol content of the various peppermint oils is somewhat at variance with the data given above. We have found the limits of value to be as follows: —

	Total menthol (not taking into account the ester content)	Ester menthol
English Oil	51 to 66%	3 to 16%
American Oil	48 „ 64%	3 „ 14%
French Oil	45 „ 69%	5 „ 21%
Japanese dementholised Oil . . .	45 „ 60%	3 „ 13%

The data supplied by the Association which relate to the menthol content of the several varieties of oil, especially those referring to free and esterified menthol cannot, in our opinion, be regarded as accurate.

Rose Oil. $d_{20^{\circ}}$ 0,855 to 0,865¹⁾; sol. p. $+ 17$ to $+ 23^{\circ}$.

¹⁾ This statement appears to have been borrowed from the French Codex, but as rose oil is often in a state of congelation at 20° it is desirable to carry out this determination at a higher temperature. At 30° (calculated for water of 15°) the limits of value observed by us ranged from 0,849 to 0,862.

Rosemary Oil. $d_{15^{\circ}}$ 0,900 to 0,920; $\alpha_D + 5$ to $+ 15^{\circ 1)}$; soluble in one-half its weight of 90 per cent. alcohol.

¹⁾ The minimum limit is not correct, many rosemary oils have a lower rotation.

Rue Oil. $d_{15^{\circ}}$ 0,833 to 0,850; α_D faintly to the right; sol. p. $+ 7$ to $+ 10^{\circ 1)}$.

¹⁾ Very many Algerian oils of rue only congeal in a freezing mixture and are faintly laevorotatory.

Sandalwood Oil. $d_{15^{\circ}}$ 0,975 to 0,985; $\alpha_D - 10$ to $- 20^{\circ}$, sap. no. should not exceed 25; santalol ($C_{15}H_{24}O$) not less than 90%; sol. at 20° 1 vol. in 5 of 70 per cent. alcohol.

Savin Oil. $d_{15^{\circ}}$ 0,909 to 0,930; $\alpha_D + 35$ to 60° ; sap. no. 107 to 125.

Star Anise Oil. $d_{20^{\circ}}$ 0,980 to 0,990; α_D faintly to the left, not to the right¹⁾; sol. p. $+ 14$ to $+ 18^{\circ}$; anethol content 80 to 90%; sol. 1 vol. in $1\frac{1}{2}$ to 6 of 90 per cent. alcohol²⁾.

¹⁾ Occasionally star anise oils are met with which are faintly dextrorotatory.

²⁾ Star anise oil is soluble with $1\frac{1}{2}$ to 3 vols. of 90 per cent. alcohol.

Thyme Oil. A thick¹⁾, reddish-brown oil; $d_{15^{\circ}}$ 0,900 to 0,950; phenol content 18 to 65%; sol. 1 vol. in 2 of 80 per cent. alcohol.

¹⁾ The adjective "thick" gives a wrong impression of the consistency of thyme oil.

Wintergreen Oil. $d_{15^{\circ}}$ 1,179 to 1,190; $\alpha_D + 0^{\circ}$ or faintly laevorotatory.

Wormwood Oil. $d_{15^{\circ}}$ 0,901 to 0,955; sol. 1 vol. in 2 to 4 of 90 per cent. alcohol¹⁾.

¹⁾ The oils at first give a solution with any proportion of 90 per cent. alcohol; but on further dilution opalescence to cloudiness frequently ensues.

Chemical Preparations and Drugs.

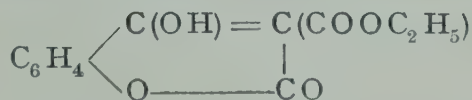
Civet. Business in this important odoriferous article was quiet with sufficient supplies, but the so-called "cheap" qualities which were imported occasionally left much to be desired. As is well known we have imported civet for over 20 years through the intermediary of a very trustworthy agent, and without exaggeration we may describe the quality offered by us as the best which arrives on the European market.

Copaiba Balsam. Evans Sons Lescher & Webb Ltd.¹⁾ give further particulars concerning the specific gravity and optical rotation of copaiba balsam oils of different origin. The values observed by them ranged within the limits set forth below: —

	$d_{15,5^{\circ}}$	α_D
1. Bahia oils	0,888 to 0,909	— 2° 42' to — 28°
2. Cartagena oils	0,895 0,896	— 30° — 40°
3. Maracaibo oils	0,900 to 0,903	— 6 to — 8°
4. Maranham oils	0,898 „ 0,905	— 1° 30' „ — 21° 40'
5. Para oils	0,886 „ 0,896	— 18° 30' „ — 32° 40'

An African balsam yielded upon distillation 48 % of oil with the constants: $d_{15,5^{\circ}}$ 0,920, $\alpha_D + 16^{\circ}$.

Coumarin. Anschütz²⁾ describes a new synthesis of coumarin. When acetylsalicylic chloride is treated with sodium malonic ester acetic ester is split off, and there is formed α -carboxethyl-benzotetronic acid or β -hydroxycoumarin- α -carboxylic ethyl ester



a compound which, when saponified with aqueous potash, is converted into β -hydroxycoumarin. From this body coumarin is obtained by substituting halogen for the OH group and by subsequent reduction with zinc-dust in alcoholic solution.

Gurjun Balsam. In one of our last Reports we mentioned a few reactions which have lately been suggested as tests for determining the presence of gurjun balsam in copaiba balsam³⁾. Lately, Deussen and Philipp⁴⁾

¹⁾ Analytical Notes 1909, Jan. 1910, 25; Comp. Report April 1908, 36.

²⁾ Liebigs Annalen 367 (1909), 202.

³⁾ Report April 1909, 42.

⁴⁾ Liebigs Annalen 369 (1909), 56.

have described a compound which has been obtained by them from gurjun balsam oil by oxidation by means of permanganate of potassium in acetone solution, and which may possibly be of use in detecting the presence of gurjun balsam. Of the neutral portions produced during the process of oxidation, those fractions which passed over *in vacuo* between 170 and 180° were treated with semicarbazide, upon which a semicarbazone $C_{16}H_{27}N_3O$, m. p. 234° (from alcohol) was formed. The authors intend to report later on the regeneration of the ketone (or aldehyde).

Heliotropin. If a change in the value of the raw material (safrol) does not occur soon, the inevitable result must be an advance in the prices of heliotropin, for which we wish to prepare our customers in good time.

Menthol. See page 88 under Peppermint Oil, Japanese.

Musk.

Exports from Shanghai from 1899 to 1909:

Year	Paris	London	New York	Germany and Austria	Total
	Catties	Catties	Catties	Catties	Catties
1909	480	161	186	60	887 ¹⁾
1908	666	37	211	9	923
1907	829	57	337	37	1260
1906	670	8	414	45	1137
1905	378	83	387	40	888
1904	722	76	366	52	1216
1903	772	157	324	73	1326
1902	751	191	360	116	1418
1901	599	154	314	105	1172
1900	790	43	219	52	1104
1899	873	180	290	148	1491

In considering the above statistics, the fact immediately attracts attention that the demand from Paris and New York has again fallen off considerably in the course of last year, the total quantity exported being, in fact, less than the total exports from Shanghai in 1905. It is true that these figures, as already mentioned by us on a previous occasion, do not give an entirely accurate view of the situation, because a considerable quantity is usually sent by post and con-

¹⁾ About 75% Tonquin, 10% Sawko and 15% Cabardine.

sequently escapes the notice of the Customs Authorities. But it may nevertheless be said with a considerable degree of accuracy that the decline in the exports, especially to the two cities which are of so much importance in the perfume trade, is due principally to the competition of artificial musk. At the same time offers from China were very abundant, with the result that it was possible, when buying, to insist upon being supplied with good quality. After the Chinese New Year (10th February) fresh arrivals at reduced prices were expected but so far there has been no notice whether this expectation of our informants has been realised. In spite of the slow demand, prices for first-class quality remained almost unchanged throughout the year and in view of the position described above, it is certainly not likely that there will be any upward change in the future. We hold a considerable stock of finest Tonquin musk, grained by ourselves, which we take the opportunity of recommending to our customers.

Ngai Camphor. We have had frequent opportunities of late years of reporting on Ngai camphor¹⁾, which is the name given to the solid parts of the essential oil of *Blumea balsamifera* D. C. roughly separated from the liquid oil. It is evident that the constitution of Ngaicamphor varies very considerably, for whereas a sample examined by us in 1895 consisted almost entirely of l-borneol, we found in another sample which we received recently from Mr. R. S. Pearson, of Dehra Dun, British India, about 75% l-camphor and only 25% oil. The crude product showed a spec. rot. $[\alpha]_D - 46,26^\circ$ in a 54,18 per cent. solution of xylene, its m. p. being 175° . After acetylation, the same xylene solution showed a saponification number of 46,4, corresponding to 13,2% of borneol. From this the borneol content of the Ngai camphor itself could be calculated at 24,4%. The separation of the two constituents was effected in the usual manner by converting the borneol into its phthalic ester acid and driving off the camphor by steam. After repeated crystallisation the two bodies were identified as l-borneol and l-camphor, with the subjoined constants: —

1. l-borneol: m. p. 204° , $[\alpha]_D - 35^\circ$ (in a 20% alcoholic solution)
2. l-camphor: m. p. 176° , $[\alpha]_D - 43,15^\circ$ (determined in a 50% xylene solution); m. p. of the oxime 119° . The solution of the oxime was dextrorotatory.

From the slight rotations of the isolated pure bodies it is to be inferred that the admixed yellow oil must be strongly lævorotatory, but it was impossible to polarise the latter, the available quantity being too small. A large sample of a similar liquid oil was examined at the time by R. Jonas, who also found, in Ngai camphor, a mixture

¹⁾ Comp. Gildemeister and Hoffmann, *The Volatile Oils*, p. 669; Report April 1908, 150; April 1909, 147.

of l-borneol and l-camphor. His investigation was published in our last April Report, to which we refer¹⁾.

Peru Balsam. Business in this important drug is becoming more and more unsatisfactory, and as the requirements of the German Pharmacopœia afford a good opportunity of showing how the article can be adulterated, reputable firms derive little satisfaction from trading in this product. Peru balsam answering the requirements of the 4th ed. of the German Pharmacopœia is being offered at almost incredible prices, and those who, like ourselves, are in the position of continuously observing the price fluctuations of the arrivals in Hamburg will support our statement. As a rule it is possible to buy Ph. G. IV. quality in the drug trade in Germany at prices below the cost of genuine original balsam imported direct. During the last few months the supplies have been very scarce, and it has been necessary to pay higher rates, a further advance of the market being expected.

Quino-Quino Balsam. Some time ago Hartwich and Jama²⁾ described a new balsam, closely allied to Peru and tolu balsam, which they designated as Quino-Quino balsam. The resin, which had been acquired by Dr. Herzog in Florida and Pampa Grande (Bolivia), is the product of *Myroxylon Balsamum* var. γ *punctatum* (Klotzsch) Baill. (N. O. Leguminosæ), a tree which grows in Peru, Southern Brazil, and Eastern Bolivia, is known in the vernacular as *Quina-Quina* and is closely related to the parent-plants of tolu and Peru balsam. According to Harms³⁾, tolu balsam is the product of *Myroxylon (Toluifera) Balsamum* var. α *genuinum* Baill. and Peru balsam that of *M. B.* var. β *Peireirae* (Royle) Baill.

The *Quina-Quina* tree yields a pale reddish-brown, very hard wood, which is used in Eastern Bolivia by builders for posts for houses, while the balsam is used as incense and as a paint. In its qualitative chemical composition it closely resembles tolu and Peru balsams. Acid no. 80,30, sap. no. 134,09, vanillin content about 0,044⁰/₀. Quino-quino balsam differs from its congeners in its lower cinnamein content (5,83⁰/₀ against 62 to 64⁰/₀ in Peru and 7,5⁰/₀ in tolu balsam), but chemically the cinnamein is the same, consisting as it does almost entirely of benzyl ester of benzoic acid with only traces of benzyl ester of cinnamic acid.

Rose "Schimmel & Co." (Red Rose). In response to numerous suggestions on the part of our customers among the perfumers, we have devoted ourselves in the course of last summer to

¹⁾ Report April 1909, 147.

²⁾ Schweiz. Wochenschr. f. Chem. u. Pharm. 47 (1909), 625, 641.

³⁾ Notizblatt des königlichen botanischen Gartens und Museums zu Berlin No. 43 (Sept. 1908).

the preparation of a rose-scent having for its basis a natural rose product, obtained by a special process in our cultivations at Miltitz. This scent reproduces perfectly and faithfully the natural odour of the fresh rose and only contains a few artificial additions required to develop the odour fully and to give it freshness. After many disappointments and much expense our work has been crowned with success and we are able to offer our customers a product which meets the highest requirements of the modern perfumer's art and which may without exaggeration be described as a novelty of the greatest importance. The preparation contains no rose oil whatsoever and reproduces the exquisite odour of fresh red roses with the greatest possible fidelity. "Schimmel & Co.'s Rose" is quite free from alcohol and differs from other similar preparations of commerce in particular by the equable and reliable character of its odour, its economy in use and its astonishing resemblance to the natural scent. We shall be pleased to supply samples free on application.

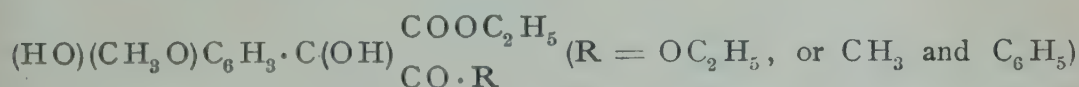
Safrol. The reduction of the stock of camphor oil in Europe has naturally brought about a corresponding increase in the prices of safrol, which have now reached a point at which the use of this important article is beginning to experience some restriction. Although our capacity for supplying safrol is considerable, we have lately been frequently compelled to decline to make offers for large quantities because in view of the present condition of the camphor oil market (see page 21) we regard it for the present as risky to make any new engagements.

Thymol. The convention among the manufacturers of thymol to which we referred in our last October Report, has in the meantime been consummated, and as a result prices, since then, have not fallen below 13.— marks. Recently there has been some change in the position, for it appears that the convention has brought certain disappointments, and it is rumoured that it has already been dissolved. It is therefore likely that the prices before long will again recede to their former level, all the more so because the raw material (ajowan seed) is being offered advantageously in large quantities, and all the preliminary conditions for a return to the old unsatisfactory state of things are therefore in existence. We have extended our plant and are in a position to compete successfully, — a fact which we beg our customers to bear in mind, especially where future delivery is required.

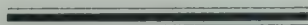
Vanillin. Guyot and Gry¹⁾ report on a new synthesis of this important odoriferous substance. They condense guajacol for a fortnight in cold glacial acetic acid solution in the presence of chloride

¹⁾ Compt. rend. 149 (1909), 928.

of zinc, with mesoxalic ester or with the α, β -diketocarboxylic esters, of which the constitution is similar, such as acetyl- or benzoyl-glyoxylic ester, afterwards heating it for several hours to about 50° . After diluting the solution with water, shaking with ether, and washing the ether with soda-solution, any unchanged guajacol is removed by means of steam and the condensation product: —



recovered in the crystalline form. By oxidation with acetate of copper at 80° these compounds can be quantitatively converted into vanilloyl-carboxylic acid, but, as regards the mesoxalic ester derivative, this can be obtained only after saponification and boiling with copper chloride. From the acid referred to, dimethyl-p-toluidin, at 170° , splits off almost quantitatively carbon dioxide and, in contradistinction to other vanillin-processes, the result is a very pale vanillin which is free from isomerides and from resinous substances. It is not recommended to employ for the purposes of synthesis the free ketonic acids in lieu of the esters, because the former are much less stable. Even when the relatively stable dioxo-succinic acid, (of which the sodium-salt is used technically in the preparation of the yellow dye known as tartrazine), is liberated from the salt by means of sulphuric acid, and this solution is shaken with guajacol, only 15% of the guajacol used is recovered in the form of vanilloyl-carboxylic acid.



Notes on recent research work concerning terpenes and terpene derivatives.

General.

In a review, going into considerable detail, of the course development of the essential oil industry during the past quarter of a century, A. Hesse¹⁾ examines the progress which has been achieved in this and allied branches of manufacture during the period under review, that is to say, since the publication of the initial researches of Wallach in terpenes and essential oils. Among the allied branches Hesse includes the manufacture of artificial odoriferous substances and scents, as well as the preparation and collection of odoriferous materials in the widest sense, the interpretation of the processes by which aromatic substances are formed in plants, the composition of those substances and, finally, their synthesis from separate constituents. Hesse was able to enlist the assistance of the majority of the firms which are industrially engaged in this branch of industry (Schimmel & Co., Heine & Co., E. Sachsse & Co., H. Haensel, Dr. Mehrländer & Bergmann, Haarmann & Reimer, Dr. Schmitz & Co., G. Lohse, and Jünger & Gebhardt), and these collaborators, in separate contributions of varying length, describe the development of their undertakings with particular regard to the scientific aspect which has been imparted to the industry by Wallach's investigations. By this means Hesse has succeeded in presenting a review which gives an extraordinarily vivid picture of the scientific, industrial and economic significance of a branch of industry in which Germany has held an undisputed lead for many years. Hesse himself agrees with the views set forth in the contributions of the firms above-named, which ascribe the enormous advance of the past decades in the first place to the systematic research-work of Wallach.

In the Wallach Jubilee publication E. Böcker²⁾ has published a voluminous article on oils free from terpenes and sesquiterpenes. In this contribution the author passes in review the entire course of development of this branch of the essential oil industry; a branch which is of special importance to liqueur-manufacturers. In order to enrich the aromatic constituents of essential oils, it has long been customary to remove from the latter those hydrocarbons which are mostly of subsidiary importance from the point of view of odour, and which, moreover, adversely affect the solubility. But whereas, generally speaking,

¹⁾ Wallach Jubilee publication (Göttingen 1909, Vandenhoeck & Ruprecht) pp. 1 to 151.

²⁾ Wallach Jubilee publication (Göttingen 1909, Vandenhoeck & Ruprecht) p. 201.

only the terpenes are thus removed, Böcker has set himself the task of also eliminating the sesquiterpenes from a large series of essential oils, and of determining the properties and constants of the resulting, highly concentrated oils. In doing this, he proceeds on the assumption that by this method it is always possible to obtain preparations of a uniform character which can be tested just as accurately in respect of quality and purity as can the original oils themselves.

Whether, and in what degree, this hypothesis is true, could only be determined, in our opinion, by broad investigations extending over a number of years. In fact, the problem would only admit of a satisfactory solution if the mode of preparing these terpene- and sesquiterpene-free oils were always the same. But the manufacturing-processes will doubtless be kept by the various makers as their special secrets, with the result that the oils will sometimes be more and sometimes less highly concentrated, and will differ proportionately from each other as regards their properties. For this reason the very ample experimental matter communicated by Böcker is only of a limited value, because he is silent on the main point, namely the preparation of the concentrated oils, apart from the fact that, (as Böcker expressly states,) it is impossible to set up generally applicable data for such a preparation, which must differ in the case of the various oils according to their peculiarities. In addition to mentioning the properties of the terpene- and sesquiterpene-free oils prepared by him, Böcker also states those of the corresponding natural oils and of the hydrocarbon-mixtures which are obtained as by-products. It will here suffice to refer for details to the original publication.

I. Kondakow¹⁾ has published a polemical treatise *Zur Geschichte der Terpene* (On the History of the Terpenes) dealing with the well-known work by O. Wallach on Terpenes and Camphors which we reviewed in a previous Report²⁾, and seeking to convince Wallach of "historical inaccuracies and other shortcomings". As the treatise does not lend itself to summarising, we must refer the curious to the original, from which every well-informed chemist will be able to form his own judgment, both as to the justification of the attacks upon Wallach and as to the controversial methods of their author. We have no doubt whatever in whose favour the judgment will be.

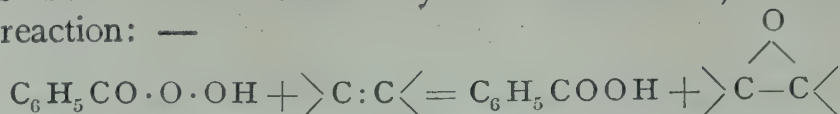
To the oxidising agents for unsaturated compounds³⁾ which have been tried recently must be added benzoylhydroperoxide $C_6H_5CO \cdot O \cdot OH$

¹⁾ Journ. f. prakt. Chem. II. 80 (1909), 455.

²⁾ Report April 1909, 107.

³⁾ Comp. Reports April 1900, 55; April 1903, 83; October 1903, 85; April 1904, 100; April 1906, 98, 99; October 1906, 101; October 1907, 154; April 1908, 178; November 1908, 171; April 1909, 137; October 1909, 167, 176.

which has been recommended by N. Prilechaew¹⁾. It gives the following reaction: —



The process of oxidation is accomplished by diluting the calculated quantity of the body which is to be treated with the solution (cooled down to 0°) of benzoyl hydroperoxide, of which the active oxygen has previously been determined by titration with iodide of potassium and sodium thiosulphate. The oxides of a series of terpenes have been prepared in this way, their properties being recorded in the table below: —

	B. p.	$d_{0^\circ}^{0^\circ}$	$d_{16^\circ}^{16^\circ}$	n_{D16°	Bodies formed as the result of hydration
Geraniol-monoxide	157 to 158° (25 mm.)	0,9716	0,9610	1,4681	A glycerol, b. p. 205 to 207° (20 mm.), is formed by the hydration
Geraniol-dioxide	180 to 183° (25 mm.)	1,0587	1,0472	1,4653	A glycerol oxide, b. p. 220° (20 mm.), m. p. 137 to 138°, is formed by the hydration
Linalool-monoxide	95° (25 mm.)	0,9660	0,9507	1,4554	[α] _D — 4,98°. A doubly unsaturated aldehyde, b. p. 120 to 122° (25 mm.), m. p. of the semicarbazone 138,5°, is formed by the hydration
Linalool-dioxide	131 to 133° (25 mm.)	1,0552	1,0423	1,4616	A glycerol oxide, b. p. 212° (25 mm.), is formed by the hydration
Citral oxide	146 to 148° (20 mm.)	1,0091	0,9740	1,4604	A glycol aldehyde, b. p. 141 to 142° (24 mm.), is formed by the hydration
Citronellal-oxide	130 to 131° (25 mm.)	0,9437	0,9344	1,4421	A glycol aldehyde, b. p. 180 to 182° (18 mm.), is formed by the hydration
Limonene-monoxide	113 to 114° (50 mm.)	0,9435	0,9303	1,4693	[α] _D — 6,76°. A glycol, m. p. 66,5 to 67,5°, is formed by the hydration
Limonene-dioxide	146 to 147° (50 mm.)	1,0471	1,0338	1,4702	[α] _D + 52,23°. An amorphous erythritol, b. p. 220° (23 mm.), is formed by the hydration
Pinene oxide	102 to 103° (50 mm.)	0,9812	0,9689	1,4708	[α] _D — 92°. Pinol hydrate, is formed by the hydration

Bibliography.

In continuation of his previous work²⁾, Brandel³⁾ has published two papers on the progress of investigation in the domain of essential oils between the years 1901 and 1903.

Analytical Notes.

In our April Report of last year⁴⁾ we gave a short reference to the experiments made by de Jong in the course of his investigation of

¹⁾ Berl. Berichte **42** (1909), 4811.

²⁾ Report April 1908, 168; November 1908, 155; April 1909, 110; October 1909, 152.

³⁾ Midland Drugg. & Pharm. Review **43** (1909), 385, 497.

⁴⁾ Report April 1909, 36.

Java citronella oils, with a view of ascertaining the most favourable conditions for determining their total geraniol content (geraniol + citronellal) by means of acetylation. De Jong's conclusions were to the effect that the process of esterification as well as the subsequent process of saponification each required two hours, and that for each 20 cc. of oil and acetic acid anhydride 2 g. of sodium acetate should be used in order to obtain accurate results, for in the case of the citronella oils examined by him he only obtained the highest values when following the rule mentioned above. Some exception may however be taken to the premises upon which de Jong's conclusions are based, seeing that the real content of total geraniol in the oils was unknown, and had to be discovered. It follows that de Jong's values may by no means correspond to the true total geraniol content, notwithstanding, or perhaps just because, they were the highest he obtained.

Proceeding from these considerations we took the constituents which together compose the total geraniol of citronella oils, that is to say geraniol and citronellal, both of the purest quality, and acetylated first of all each of the bodies by itself and next mixtures of the two bodies with pinene, observing approximately the same proportions as occur in the natural Java citronella oil. By altering the length both of the acetylation and the saponification process as well as the proportions of sodium acetate, we were able to ascertain the conditions under which the values can be found which correspond most closely in each case to the real constitution. From the results printed below in tabular form it will be seen that although de Jong has hit upon the proper measure of time (two hours each), for the esterification and the subsequent saponification-process, he has not used a sufficiency of sodium acetate; 2 g. of this material to each 20 cc. of oil and anhydride being too little. According to our tests with mixtures of known content the true proportion of geraniol + citronellal can only be ascertained when 4 g. sodium acetate is employed. This result is not quite in concord harmonised with the methods at present in use in the acetylation of essential oils. At present, the method laid down by us¹⁾, is as follows: 10 cc. of the oil, mixed with an equal volume of acetic anhydride are boiled uniformly with about 2 g. of dry sodium acetate for one hour in a small flask provided with a condensing tube which is ground into the neck of the flask, and, after washing, are also saponified for one hour only. We have satisfied ourselves by voluminous experiments that the conditions of time and quantity described above are correct for the quantitative estimation of the following alcohols, viz., geraniol, borneol, menthol, and santalol, but that the conditions which should be applied in the case of terpineol are different, whereas

¹⁾ Comp. Gildemeister and Hoffmann, *The Volatile Oils*, p. 194.

linalool cannot be quantitatively acetylated at all¹⁾. But the table printed below further shows that in the case of the alcohols mentioned first it does not matter whether the esterification and the saponification are continued for one or for two hours, as the results are not materially altered thereby. The proportions of sodium acetate employed also have less effect upon the course of the reaction in the case of these alcohols than in that of citronellal.

Sodium Acetate, grams:		1,0		2,0		2,5	
Time of acetylation:		1 h.	2 h.	1 h.	2 h.	1 h.	2 h.
Time of Saponification							
Citronellal	{ 1 h.	79,7 %	94,2 %	82,1 %	96,9 %	91,0 %	103,8 %
	{ 2 „	79,3 %	94,8 %	82,4 %	99,8 %	95,9 %	104,4 %
Geraniol	{ 1 „	98,1 %	97,7 %	97,8 %	95,1 %	97,5 %	95,7 %
	{ 2 „	98,1 %	97,9 %	97,7 %	96,7 %	98,2 %	95,8 %
40 % Geraniol . 20 % Pinene . . 40 % Citronellal	{ 1 „	70,6 %	76,2 %	73,65 %	78,8 %	74,0 %	79,0 %
	{ 2 „	70,8 %	76,9 %	75,0 %	80,3 %	74,6 %	79,9 %
Borneol	{ 1 „	99,0 %	99,6 %	99,0 %	99,8 %	99,1 %	99,45 %
	{ 2 „	99,1 %	99,5 %	99,3 %	99,7 %	99,5 %	99,0 %
Menthol	{ 1 „	100,0 %	100,0 %	99,5 %	100,0 %	99,5 %	99,75 %
	{ 2 „	99,6 %	99,6 %	99,75 %	99,6 %	99,25 %	99,7 %
Santalol	{ 1 „	97,9 %	99,6 %	99,2 %	99,75 %	99,4 %	99,5 %
	{ 2 „	98,1 %	99,6 %	99,4 %	100,0 %	99,25 %	99,85 %

The behaviour of natural oils of citronella is similar to that of artificial mixtures of citronellal, geraniol and pinene. Ceylon oils, with their low citronellal content, show no material difference whether they are acetylated and saponified for one or for two hours, at any rate, such differences are so minute that they may also be regarded as experimental errors. But in the case of Java oils, of which the constitution is about similar to that of our artificial mixtures, the results depend upon the quantity of sodium acetate added and upon the time devoted to esterification and saponification. The same applies to the oil of *Eucalyptus citriodora*, which consists chiefly of citronellal. A sample of this oil after two hours' acetylation was found to consist of 100 % alcohol of the formula $C_{10}H_{18}O$, as compared with only 84 % after one hour's heating. The high value recorded in the former case may perhaps be due to the presence of other aldehydes of lower molecular weight which, in the course of the acetylation process, underwent an alteration which caused them to increase the ester-number on subsequent saponification. This surmise is supported by the recent investigations of Semmler²⁾ which show that aldehydes in the con-

¹⁾ Comp. Report April 1907, 119.

²⁾ Berl. Berichte 42 (1909), 584, 963, 1161, 2014; Reports April 1909, 128 October 1909, 183.

stitution of which at least one H-atom is found in an adjacent position to the CHO-group, react with acetic acid anhydride in the enolic form.

Similar experiments with natural oils confirm us in insisting upon the desirability of adhering to the proportional quantities recommended by us, (2 g. sodium acetate for every 10 cc. of oil and acetic acid anhydride,) because it is only under these conditions that results are obtained which most closely approximate to the actual content. In the case of all oils containing citronellal it is further desirable both to acetylate and to saponify for two hours each; with other oils, one hour will suffice for each manipulation.

Grams Na-acetate	Duration of acetyl.	Duration of sapon.	Ceylon Citronella Oil	Java Citronella Oil	Oil of <i>Eucal.</i> <i>citriod.</i>	New Guinea Citronella Oil
2	1	1	57,6 ⁰ / ₀	80,0 ⁰ / ₀	84,0 ⁰ / ₀	78,1 ⁰ / ₀
2	2	1	58,4 ⁰ / ₀	85,3 ⁰ / ₀	100,1 ⁰ / ₀	85,1 ⁰ / ₀
2	1	2		81,5 ⁰ / ₀		
2	2	2		87,1 ⁰ / ₀		

In connection with the above we have made a series of other experiments in order to determine, among other things, whether in the process of acetylation by means of the small flask introduced and used by us¹⁾, there occurs any loss by evaporation during boiling. With this object in view we acetylated mixtures of 50⁰/₀ pinene with 50⁰/₀ menthol, 50⁰/₀ borneol and 50⁰/₀ geraniol respectively; first without taking any special precautions and using our ordinary flask provided only with a condensing tube; and, secondly, with a reflux-condenser. In every instance, however, we found only the calculated quantity of 50 to, at most, 50,7⁰/₀ of terpene-alcohol. Nor is there any ground for the fear that during the washing-out of the contents of the flask with water certain constituents of the acetylated oil might dissolve, and thus disturb the original proportions of the mixture, for the tests which we applied to elucidate this question showed that the result is in no wise affected whether a solution of 50⁰/₀ menthyl or bornyl acetate in pinene is or is not repeatedly washed with water before being saponified, from 49,7 to 50,2⁰/₀ of ester being recovered in every case.

R. A. Cripps and J. A. Brown²⁾ have worked out a method for determining the essential oil content of spices and aromatic drugs. On the one hand they determined the total content of volatile substances by drying 1 to 2 g. of the material at 135° in a current of dry air up to 1 hour, and on the other they ascertained the water content of a sample of 0,5 g. by Dupré's method. The difference indicates

¹⁾ Gildemeister and Hoffmann, *The Volatile Oils*, p. 195.

²⁾ Analyst **34** (1909), 519. Through Chem. Zentralbl. **1910**, I. 691.

the essential oil content of the material concerned. Cripps and Brown by this method, have determined the essential oil content of a whole series of spices. The table attached to their paper shows, however, that the contents thus ascertained were partly below the normal yields, which may be due to oxidation processes and the consequent increase in the weight of the crude material during the drying.

In the course of years various investigators¹⁾ have recommended that in the testing of essential oils the refractive index should be considered. Parry²⁾ has recently endorsed these views. According to him, this constant is just as valuable in detecting adulterations as are the specific gravity and the optical rotation. It may be capable of rendering particularly valuable service in testing the separate fractions of an essential oil, in which case, by comparing the results with those obtained with a genuine oil, sophistications may easily be recognised. On these grounds Parry regards the determination of the index of refraction as a very practical measure. At the same time he gives the indices of refraction of a series of oils, constituents of oils, and adulterants as determined by him in the course of several years' experience, and promises the publication of such indices for the different fractions of certain essential oils.

The result of our own observations on the refractive index of essential oils during the past ten years has failed to convince us of the importance of this factor. Only in a very few sporadic instances, as, for example, in that of geranium oil, and possibly also rose oil, does this constant give really useful pointers, but as a general rule it expresses less than do the old-established measures of value, such as specific gravity, optical rotation, etc. This our statement is based upon a very voluminous collection of data, which we intend to publish occasionally elsewhere.

In testing the separate fractions of an oil, the index of refraction, however, may under certain conditions render great service.

Physical Notes. .

In our last Report we made a reference to a paper by v. Rechenberg³⁾ in which he called attention to a source of error in boiling-point determinations under diminished pressure which had thus far

¹⁾ Gladstone, *Journ. chem. Soc.* II. **10** (1872), 1; *Abstraction Jahresber. d. Chem.* **1872**, 813; *Pharmaceutical Journal* III. **2** (1872), 687, 704, 745; Kremel, *Pharm. Post* **21** (1888), 789; Biel, *Pharm. Zeitschr. f. Russland* **1890**; Marpmann, *Pharm. Zentralh.* **33** (1892), 209; Hartwich, *Schweiz. Wochenschr. f. Chem. u. Pharm.* **33** (1899), 329; *Apotheker Ztg.* **14** (1899), 584; Utz, *ibid.* **15** (1900), 441, 453; **16** (1901), 742.

²⁾ *Chemist and Druggist* **76** (1910), 178.

³⁾ *Journ. f. prakt. Chem.* II. **79** (1909), 475; Report October **1909**, 157.

escaped attention. According to v. Rechenberg, the reason why inaccurate data as to pressure have been given lies in the insertion in the wrong place of the manometer, which ought to be directly connected with the boiling flask. Von Rechenberg also explained that the distillations in an exceptionally high vacuum, which had been carried out by Krafft and his pupils had produced inaccurate results owing to the faulty arrangement of the apparatus, as could easily be seen by comparing these results with those of exact experiments—of other investigators. Krafft¹⁾ opposes this view in a paper published under the title “On Boiling as a means of overcoming Gravitation, and on Distillation *in vacuo*”. In this paper, following the example of Hansen²⁾, Krafft enters into details of little importance, but he fails to meet the essence of v. Rechenberg’s demand, namely that the pressure should be determined of those vapours of which the temperatures are given. Nor does Krafft explain why his results, insofar as they admit of comparison at all, should differ so greatly from the exact results given by other investigators. In his criticism, entitled “Krafft’s Boiling-point Determination and Distillation Theory”, von Rechenberg³⁾ lays particular stress upon this point, and discusses Krafft’s hypothesis that, in its essence, boiling is the conquest of gravitation. Krafft regards gravitation as an obstacle to the removal of saturated vapours of very low tension from bodies with a high boiling point, but von Rechenberg explains that the cause of this must be sought in the condensaton of the vapour which is the result of external cooling.

Pharmaco-physiological Notes.

In our previous Report⁴⁾ we mentioned briefly that when camphor is internally administered to dogs, it leaves the organism in combination with glucuronic acid. It has been known for some time that borneol behaves similarly. The borneol glucuronic acids, of which few details have been known thus far, have recently been described by J. Hämäläinen⁵⁾. This author obtained the acids after internal administration to rabbits by isolating them from the urine. The results are summarised in the subjoined table: —

	M. p. of the compound containing water of crystallisation.	M. p. of the an- hydrous compound	Spec. rot.
rac. Borneol glucuronic acid .	94 to 95°	163 to 165°	— 47,93°
rac. Isoborneol glucuronic acid	104 to 106°	162 to 163°	— 42,62°
l-Borneol glucuronic acid . .	96 to 97°	162 to 163°	— 69,03°
d-Borneol glucuronic acid . .	94 to 95°	164 to 165°	— 37,02°

¹⁾ Journ. f. prakt. Chem. II. 80 (1909), 242.

²⁾ Journ. f. prakt. Chem. II. 80 (1909), 449.

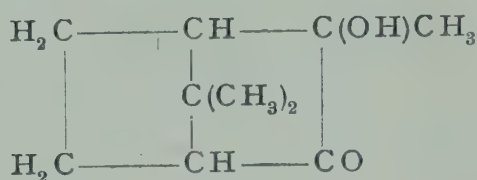
³⁾ Journ. f. prakt. Chem. II. 80 (1909), 547.

⁴⁾ Report October 1909, 163.

⁵⁾ Skand. Arch. f. Physiol. 23 (1909), 86; from a reprint kindly sent to us.

Some time ago E. Rimini¹⁾ discovered that carone and fenchone behave similarly. Carone is oxidised in the animal organism into hydroxycarone, which in its turn is eliminated in the urine in the form of carone glucuronic acid, and may be isolated from the former by boiling with dilute sulphuric acid. When the boiling is continued for a long time, however, the carone is converted into ketoterpine and carvacrol.

The behaviour of fenchone is akin to that of carone. It passes off in the urine in the form of fenchone glucuronic acid, which, when boiled with dilute sulphuric acid, decomposes into glucuronic acid and hydroxyfenchone (m. p. 89°; b. p. 250 to 252°). Rimini, who prefers Wallach's fenchone-formula, ascribes the following formula to hydroxyfenchone.



The author has also prepared the phenylhydrazone of fenchone by heating pernitrosofenchone with phenylhydrazine hydrochloride and sodium acetate in alcoholic solution. The body appears as a yellow oil, b. p. 202 to 203° (18 mm.). Pernitrosofenchone is obtainable in almost quantitative yield from fenchone oxime by treating it with nitrous acid in a solution of acetic acid.

Camphoquinone (from *is*onitroso-camphor, sodium sulphite and glacial acetic acid), upon being heated in a melting tube with hydrosulphide of ammonium yielded, in addition to camphor, bornyl disulphide and trisulphide, from which, by distillation, thiocamphor and thioborneol were obtained. Precisely analogous is the behaviour of fenchone, from which thiofenchone (b. p. 207 to 208°) and thiofenchyl alcohol were prepared.

In the case of thujone²⁾ the yield of pernitroso-compound is rather smaller, being about 80 per cent. By reacting upon pernitroso thujone with concentrated sulphuric acid *is*othujone is formed (b. p. 224° [741 mm.]; m. p. of the semicarbazone 208 to 209°; of the oxime 119°). Carone oxime gives with nitrous acid about 35% pernitroso-compound, which, with concentrated sulphuric acid, forms carvenone. The pernitroso-derivatives of the terpenones, when heated for a short time in the water-bath with hydrosulphide of ammonium, yield the corresponding thioketones. Thus, pernitroso fenchone gives thiofenchone, pernitroso menthone a mixture of menthone and thio-menthone. Thujone apparently gives thio-isothujone.

¹⁾ Gazz. chim. ital. **39** (1909), II. 186; from a reprint kindly sent to us.

²⁾ Gazz. chim. ital. **39** (1909), II. 196; from a reprint kindly sent to us.

The suspicions which were cast upon anethol in France on the occasion of the prohibition of absinthe, have induced J. Piot¹⁾ to call attention to the absolute non-toxicity and the valuable therapeutic properties of anethol. Several investigators²⁾ have already shown that anethol is non-poisonous. On the other hand it has proved valuable as a stomachic, digestive, diuretic, carminative and antiseptic. Apart from its use as a mouth-wash, it has been recommended as an antiseptic in tuberculosis, being exhaled through the lungs, and being on that account reputed to act antiseptically upon these organs. Piot concludes that there are no valid reasons for objecting to the employment of anethol in liqueur manufacture.

Phyto-physiological Notes.

Some time ago Mirande as well as Guignard³⁾ made the remarkable discovery that certain anæsthetics have the power of liberating hydrocyanic acid, mustard oil and methyl salicylate from plants in which these bodies are held in glucoside-like combinations. Heckel⁴⁾ now reports that coumarin also is liberated from glucoside-like compounds by anaesthetics. For instance: chloroform and ethyl ether immediately set free coumarin from the leaves of *Liatris spicata*; in the case of *Anthoxanthum odoratum* similar liberation takes only place after 10 minutes' action. But when, a mixture of methyl and ethyl chloride is employed as an anaesthetic, the separation of coumarin from *Anthoxanthum* is effected at once. In the case of *Melilotus officinalis*, chloroform or ethyl ether require about 2 hours, a mixture of methyl and ethyl chloride 15 minutes. It is noteworthy that under normal conditions the coumarin-odour does not assert itself until the plant has been dried. *Diplotaxis tenuifolia*, under the influence of the methyl-ethyl-chloride mixture yields immediately an odour of mustard oil, which, however, differs from that of ordinary oil of mustard.

In a previous report we discussed the researches of Goris and Ducher⁵⁾ on the occurrence of methyl salicylate in the roots of various varieties of *Primula*. The authors ascribed the ester-odour which became perceptible even when the root was merely rubbed, to a process of fermentative decomposition. In the meantime Goris and Mascré⁶⁾ have ascertained that the root of the primrose species known

¹⁾ Journ. de la Parfumerie et Savonnerie 22 (1909), 234.

²⁾ Comp. Report April 1904, 104.

³⁾ Compt. rend. 149 (1909), 91, 140; Report October 1909, 164.

⁴⁾ Compt. rend. 149 (1909), 829.

⁵⁾ Bull. des Sciences pharmacol. 13 (1906), 536; Report April 1907, 127.

⁶⁾ Compt. rend. 149 (1909), 947.

as *Primula officinalis* Jacq. contains a ferment, primverase, which has the power of splitting-up two glucosides, primverin and primulaverin, which have also been discovered in the root by the authors. This ferment is also present in other parts of the plant, as well as in many other *Primulaceæ*. Pure primverin occurs in white crystals, m. p. 172 to 173°, specif. rot. — 60,24°. Pure primulaverin forms white needle-shaped crystals, m. p. 160 to 161°, specif. rot. — 66,86°. Both glucosides, in aqueous solution, slightly decompose Fehling's solution. When boiled with dilute sulphuric acid an anise-like odour becomes perceptible.

Up to the present it has been generally held that the hydrolysis of salicin by the aid of emulsin did not proceed mono-molecularly. C. S. Hudson and H. S. Paine¹⁾ have lately shown that this is an erroneous view. These investigators showed that the reaction does proceed mono-molecularly, always presuming that in the polariscopic determination of the glucosides which are formed in the process of hydrolysis the multirotation be taken into account. Earlier investigators had overlooked this point and had therefore arrived at incorrect results. The liquid which is to be polarised must in every case be rendered faintly alkaline in order that the glucose may show the proper rotation. The authors also discovered that the glucoside of salicin is not α -, but β -glucose.

Hydrocarbons.

Menthene. When chlorocarvene (I), which is formed when carvenone is treated with phosphorus pentachloride, is reduced with sodium and alcohol, the result, according to Semmler²⁾, is carvenene (II). It was therefore to be expected that pulegone would, by an analogous process, through its chloride (*isoterpinolene* chloride) (III) yield a hydrocarbon, *isoterpinolene* (IV)³⁾. But in actual practice the reaction takes a different course, of which the principal product is a mixture of Δ^3 - and Δ^4 ⁽⁸⁾-menthene. By treating pulegone with phosphorus pentachloride Auwers obtained 3-chloro*isoterpinolene* (III), which has already been described by Klages, and which, when dissolved in ten times its vol. of alcohol was reduced by twice its weight of sodium. Among the products of reaction was Δ^4 ⁽⁸⁾-menthene (dihydroterpinolene) (V), a hydrocarbon previously obtained by Wallach⁴⁾ by another method. For purposes of identification the author prepared the nitrosochloride described by Wallach, which, when liquid, has a blue colour, volatilises with steam,

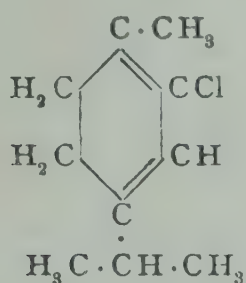
¹⁾ Journ. Americ. chem. Soc. **31** (1909), 1242.

²⁾ Berl. Berichte **41** (1908), 4474; Report April 1909, 122.

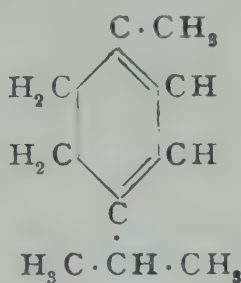
³⁾ Auwers, Berl. Berichte **42** (1909), 4895.

⁴⁾ Liebigs Annalen **360** (1908), 72; Report November 1908, 167.

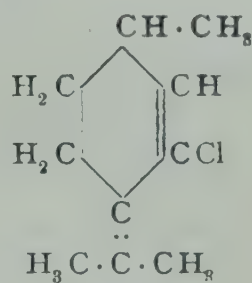
and melts at 103 to 104° when recrystallised from methyl alcohol. The reaction mixture also contained ordinary Δ^3 -menthene (VI), which was also identified by the nitrosochloride (m. p. 143 to 144°). It is not possible to decide whether, in addition to these two hydrocarbons, Δ^2 -menthene occurs among the products of reaction, because so very little is as yet known of this hydrocarbon. It is possible that the mixture may also contain *isoterpinolene*, but this could not be proved with certainty.



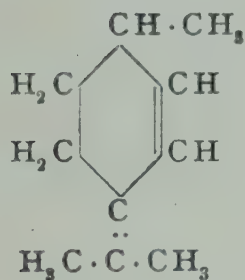
I.



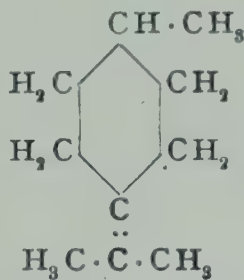
II.



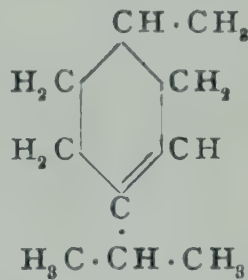
III.



IV.



V.



VI.

Camphene. Some years ago we announced that Schindelmeiser¹⁾ had found that Siberian pine-needle oil contained a powerfully lævorotatory camphene. Recently the same observation has been made by P. Golubeff²⁾. The latter prepared l-camphene by carefully fractionating the oil and allowing the constituent in question to freeze out. The recrystallised compound possessed the following properties: m. p. 50°, b. p. 159 to 160°, α_D — 92,37°. It had an agreeable odour and was very volatile. When treated with glacial acetic and sulphuric acids by Bertram and Walbaum's method, it yielded isobornyl acetate; 20 per cent. of the camphene employed giving no reaction. When the oil was treated directly with glacial acetic and sulphuric acids, isobornyl acetate was likewise formed, and the mother-liquor, after saponification, was found to contain i-camphene and cymene.

¹⁾ Comp. Report October 1903, 86.

²⁾ Journ. Russ. phys. chem. Soc. 41 (1909), 1004. Through Chem. Zentralbl. 1910, I. 30.

Pinene. Since Tilden, in 1875¹⁾, discovered pinene nitrosochloride numerous methods have been proposed for the preparation of this compound. In the main their object is to prepare the nitrosyl chloride in the easiest possible manner, and at the same time of the highest possible degree of purity, and to ascertain the best conditions for mixing the reagents. Tilden arrived by a difficult method from nitrohydrochloric acid, *via* nitrosyl sulphuric acid with sodium chloride and pure nitrosyl chloride. With this body (at first undiluted, afterwards in a chloroform solution and under strong cooling), he acted upon pinene (subsequently also in a chloroform solution). Wallach²⁾ began by employing ethyl nitrite, which is easily prepared, and a solution of pinene in glacial acetic acid, until finally he replaced the ethyl compound by the more manageable amyl nitrite.

Some time ago Dr. Paul Ehestädt, of Pankow, near Berlin, informed us in writing that he had obtained a satisfactory yield of pinene nitrosochloride by the following very simple method: "Oil of turpentine is diluted with its own volume of petroleum ether, glacial acetic acid, or preferably, ether. Into this solution, which can be readily cooled with ice, the gases are passed which are generated by allowing concentrated solution of sodium nitrite to drop very slowly into 32 per cent. crude hydrochloric acid ($1\frac{1}{2}$ times the theoretical quantity) — not *vice-versâ*, for in that case the yield is very slight. By the time when about one-third of the sodium nitrite solution is used up, beautiful crystals of pinene nitrosochloride begin to separate out, and at the conclusion of the process the mixture forms a paste. It is said that the method is especially adapted to the preparation of large quantities of the compound.

We have tried Ehestädt's method, and are able to confirm that it is indeed very simple. With pure pinene the yield of nitrosochloride is at least as large as by Wallach's method. This is shown in the subjoined table, in which we give (although not in a complete form) the quantitative output of nitrosochloride obtained by us with the various methods.

Yield of pinene nitrosochloride by the different methods of preparation.

Material	α_D	Tilden (CHCl_3)	Ethyl Nitrite	Amyl Nitrite	Ehestädt
1. Pinene	$+11^\circ 10'$	10 %	31,4 %	30,0 %	37,5 %
2. "	$+40^\circ 23'$	—	4,0 %	4,0 %	4,6 %
3. "	$-33^\circ 42'$	—	11,0 %	9,0 %	10,0 %
4. "	inactive ³⁾	—	20,0 %	—	22,0 %

¹⁾ Journ. chem. Soc. (2) 13, 1875, 514 and 518. Through Jahresber. d. Chem. 28 (1875), 390.

²⁾ Liebigs Annalen 253 (1889), 251.

³⁾ This inactive pinene was prepared by mixing proportionate quantities of the pinenes 2 and 3.

Incidentally, the figures given above confirm the fact, which had already been observed by Tilden, that pinenes of high rotatory power do not yield so high a percentage of nitrosochloride as do pinenes which have a lower rotation or which are inactive. Several explanations of this phenomenon have been given. As mentioned by us on a previous occasion¹⁾ the discoverer of the nitrosochlorides himself has drawn the conclusion from the optical inactivity of pinene nitrosochloride ($C_{10}H_{16}NOCl$)₂, (which body was first recognised as a bimolecular compound by Baeyer²⁾), that the proportions of d- and l-pinene which enter into the reaction are always equal, and that therefore the yield is largest when the original hydrocarbon itself is inactive, *i. e.*, when it consists of corresponding proportions of d- and l-pinene. When there is a definite rotation in either direction, the nitrosochloride of the active pinene is formed, but this body is unstable, and in its tendency to assume the stable, inactive, form one-half of it is inverted and its rotation reversed, and this action is attended by the liberation of so much heat that a considerable part of the nascent nitrosochloride is again decomposed in the act of generation. Hence, owing to increased inversion, the heat generated increases in proportion with the activity of the pinene employed and the yield of nitrosochloride diminishes correspondingly. We have recently expressed our own theory of these phenomena in another publication³⁾ to which a reference will here be sufficient.

In the course of our extended experiments we have also applied Ehestädt's method to the determination of small quantities of pinene in presence of limonene, especially in cases where by Wallach's method no nitrosochloride was obtainable⁴⁾.

In such cases, however, Ehestädt's method, too, gave no better results. As an example we may quote a case in which it was sought to ascertain whether the presence of pinene in lemon oil can be detected when 10% of the oil is distilled off in a Ladenburg flask, in accordance with the usual practice. Here the method did not show any advantage over others which are more familiar. In order, however, to render the determination of pinene in mixtures, as for instance with limonene, as sensitive as possible, we attempted to convert any α -pinene which might be present, into pinonic acid or β -pinene into nopinic acid, and in these experiments we obtained more satisfactory results. Our method was as follows: 5 cc. of the fraction under examination was shaken up mechanically for about 3 hours with a mix-

¹⁾ Report October 1904, 110.

²⁾ Berl. Berichte 28 (1895), 648.

³⁾ Report November 1908, 64.

⁴⁾ Comp. Report October 1909, 165. Gildemeister and Köhler, Wallach Jubilee publication, Göttingen 1909, p. 432.

ture of 12 g. powdered potassium permanganate, 2,5 g. sodium hydroxide, 200 g. water and about 500 g. ice. The mixture was then super-saturated with carbon dioxide gas and distilled with steam for the purpose of removing any non-oxidised portions. After filtration, the liquid was evaporated in a current of carbon dioxide gas to about 200 cc. and repeatedly extracted with chloroform to remove impurities. Gradually, after still further evaporation, a crystalline incrustation separated out from the solution; this was removed by suction and treated with dilute sulphuric acid, when a readily crystallising body (m. p. 125°) separated off, which proved to be nopinic acid. This was converted by oxidation into nopinone, the characteristic odour of which is unmistakable. The experiment shows the method (*i. e.* oxidation) to be applicable in detecting the presence of β -pinene in the initial 10% of pure oil of lemon if the fraction in question has been obtained according to our distilling-method. In spite of frequent repetition of the experiment, α -pinene was not traceable with equal certainty, because the mother-liquor of the sodium nopinate, after adding dilute sulphuric acid and treating with ether, yielded only traces of a semicarbazone, which were insufficient for exact identification.

To our previous communications on experiments in reduction in the terpene series¹⁾ we are now able to add a new one, which is taken from a treatise recently published by Vavon²⁾. This investigator reduced terpene hydrocarbons by shaking them with platinum black in a hydrogen-atmosphere. From pinene from Aleppo turpentine oil ($[\alpha]_{D15^{\circ}} + 48,3^{\circ}$), he obtained a hydrocarbon $C_{10}H_{18}$ with the following properties: b. p. 166° (755 mm.), sol. p. about -45° , $d_{15^{\circ}}^{15^{\circ}} 0,861$, $[\alpha]_D + 22,7^{\circ}$. French oil of turpentine yielded the same body, but with this difference that the specif. rot. was $-21,3^{\circ}$. From camphene (m. p. 55° ; $[\alpha]_D - 80^{\circ}$) Vavon also obtained a hydrogenated hydrocarbon $C_{10}H_{18}$, m. p. 87° . Limonene ($[\alpha]_D + 121,3^{\circ}$) absorbed 4 atoms of hydrogen, and in the course of this process a hydrocarbon was formed possessing the following constants: b. p. 169° , $d_{15^{\circ}}^{15^{\circ}} 0,803$, $[\alpha]_D \pm 0$.

In a previous publication Henderson, working together with Agnew³⁾, had described the formation of i-pinol hydrate from i-pinene by oxidation with mercuric acetate. More recently, Henderson, in collaboration with W. J. S. Eastburn⁴⁾, discovered that optically active

¹⁾ Report October 1903, 83; April 1904, 107; October 1907, 113; October 1909, 186.

²⁾ Compt. rend. 149 (1909), 997.

³⁾ Journ. chem. Soc. 95 (1909), 289; comp. Report October 1909, 167.

⁴⁾ Journ. chem. Soc. 95 (1909), 1465.

pinene also, when treated with mercuric acetate, yields only i-pinol hydrate. Thus, d-pinene from Burmese oil of turpentine ($[\alpha]_{D20^\circ} + 34,1^\circ$), d-pinene from American oil ($[\alpha]_{D20^\circ} + 13,0^\circ$), and l-pinene from French oil, ($[\alpha]_{D20^\circ} - 39,2^\circ$) all yielded i-pinol hydrate (m. p. 131°). The readiness with which pinene reacts with mercuric acetate was used by the authors as a means of identifying the hydrocarbon. By this method they succeeded in determining the presence of d- α -pinene in a small quantity of a dextrorotating fraction, (b. p. 156 to 157 ; $d_{4^\circ}^{20^\circ} 0,8598$; $[\alpha]_{D20^\circ} + 28,4^\circ$), which they had isolated from a large quantity of Russian oil of turpentine. In a Swedish oil of turpentine, however, they were unable to detect any pinene.

W. Smirnoff¹⁾ has investigated more closely the inversion (long since known) of pinene into dipentene by heating it with dilute sulphuric acid. The author boiled a mixture of 5 cc. l-pinene, 15 cc. alcohol, 0,6 cc. water and 1 cc. 2 per cent. sulphuric acid, cooling down the mixture at intervals to 18 to 20° , in order to examine its chemical behaviour. He observed in the course of this manipulation that the rotation first increased and afterwards, by degrees, receded to 0° . The highest index of rotation was reached after the mixture had been heated for $2\frac{1}{2}$ hours; the reaction-mixture contained, in addition to intact pinene, a compound $C_{10}H_{17}OC_2H_5$ with the following constants: b. p. 216 to 217° (740 mm), $d_{17,5^\circ}^{20^\circ} 0,9010$, $\alpha_D - 66,95^\circ$, $n_{17,5^\circ}^{20^\circ} 1,4649$. The same compound was isolated from another reaction-mixture, the result of 4 hours' heating. As no l-limonene was detected in either case, the author concludes that the transformation of pinene into dipentene does not take place, in the initial stages, over l-limonene, as Flawitzky believed to be the case.

By separating hydrochloric acid from pinene nitrosochloride by means of sodium methylate, Deussen and Philipp²⁾ obtained a body $C_{11}H_{19}NO_2$, m. p. 101 to 102° , on which they intend to report later.

Terpinolene. So far, attempts to produce a terpinolene free from foreign admixtures had not been successful, on account of the readiness with which the substance is isomerised by acids, under displacement of the double bond (formation of terpinene)³⁾.

With the object of preparing a pure terpinolene, Baeyer⁴⁾ took as his crude material terpinolene tetrabromide, which he reduced with

¹⁾ Journ. Russ. phys. chem. Soc. **41** (1909), 996. Through Chem. Zentralbl. **1910**, I. 30.

²⁾ Liebigs Annalen **369** (1909), 62.

³⁾ Comp. Wallach, *Terpene und Campher*, Leipzig 1909, p. 309.

⁴⁾ Berl. Berichte **27** 1894), 448.

zinc dust and glacial acetic acid, but this method frequently yielded a terpinolene which was undoubtedly contaminated with carvenene (α -terpinene). In order to avoid this impurity, which, for the reasons abovenamed, is ascribable to the presence of the acid, Semmler¹⁾ reduced terpinolene tetrabromide with zinc dust and alcohol, and by this means obtained a terpinolene possessing the following properties: b. p. 67 to 68 (10 mm.), d_{20}° 0,854, n_D 1,484, mol. refr. found, (in rough figures) 45,5, calc. for $C_{10}H_{16}/\sqrt{2}$ 45,2. From the above physical constants, Semmler thinks that the presence of terpinolene in the terpinenes may be inferred, because in the case of carvenene (α -terpinene) the refractive index was found to be 1,4991, and a lower figure, therefore, indicates contamination with terpinolene.

Terpinene. In our last Report we discussed the synthesis of α -terpinene from o-cresol which has been carried out by Auwers²⁾, and we mentioned the said investigator's opinion that his α -terpinene was not identical with Semmler's carvenene³⁾. The latter has now published the result of a fresh investigation of carvenene⁴⁾ in which he adheres to the view he had previously expressed that carvenene is a pure $\Delta^{1,3}$ -dihydrocymene (α -terpinene), proving his contention by oxidation to α, α' -dihydroxy- α -methyl- α' -isopropyladipic acid⁵⁾. He further gives it as his opinion that the synthesis of α -terpinene from o-cresol which has been carried out by Auwers (*loc. cit.*) has only complicated still further the whole question of terpinene, especially because Auwers has not been successful in obtaining α, α' -dihydroxy- α -methyl- α' -isopropyladipic acid directly from his hydrocarbon. Semmler therefore does not see why his carvenene should contain less terpinene than Auwers' hydrocarbon. Auwers replies to this objection⁶⁾ that on the contrary the acid in question had been obtained from the hydrocarbon in a comparatively high proportion. Semmler's view as to the further complication of the terpinene-problem by Auwers' synthesis, the latter says, is not in accordance with the facts, because the synthetic product from o-cresol is not a new isomeride.

Wallach⁷⁾ is likewise unable to share Semmler's views as to the confusion which is alleged still to exist on the terpinene-question. He refers to his earlier publications as showing that the structure of

¹⁾ Berl. Berichte 42 (1909), 4644.

²⁾ Berl. Berichte 42 (1909), 2404; Report October 1909, 172.

³⁾ Comp. Report April 1909, 122.

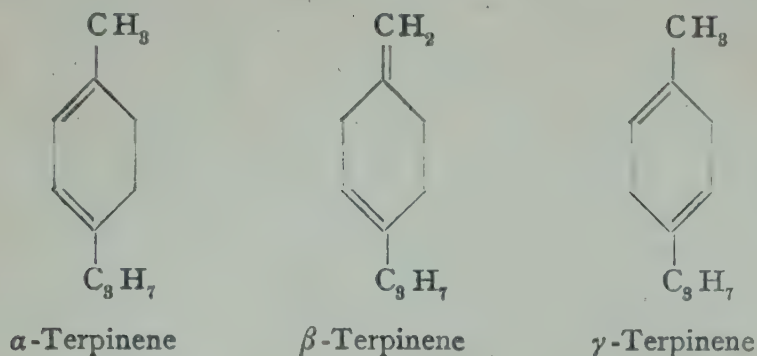
⁴⁾ Berl. Berichte 42 (1909), 4171.

⁵⁾ Comp. Report October 1909, 170.

⁶⁾ Berl. Berichte 42 (1909), 4427.

⁷⁾ Nachr. K. Ges. Wiss. Göttingen, 1909, Meeting of 4. December 1909.

the three terpinenes which are known up to the present is as follows¹⁾: —



The fact that Semmler is introducing α -terpinene by the name of carvenene, and β -terpinene by that of *isocarvenene* is not likely, Wallach avers, to place the subject in a clearer light. In any case, in the present state of research, the name terpinene should not be used without a prefix, to designate a particular hydrocarbon.

Semmler prepared his carvenene by reducing the chloride $C_{10}H_{15}Cl$ which, he states, he was able to obtain in good quantitative yield and of exceptional purity by the conversion of carvenone with phosphorus pentachloride²⁾. Neither Wallach nor Auwers were able to obtain an equally good yield when preparing this body; its purity, too, left much to be desired.

Caryophyllene. In continuation of his earlier researches, to which we have made occasional reference³⁾, Deussen⁴⁾ has published another paper on caryophyllene and its derivatives. The nitrolamine base obtained by treating caryophyllene nitrosate with benzylamine, (which base Schreiner and Kremers have termed β -caryophyllene nitrolbenzylamine,) is according to the latest investigations of Deussen a derivative of α -caryophyllene. The m. p. of α -caryophyllene nitrolbenzylamine lies between 126 and 128° ; while the, probably inactive, α -caryophyllene nitrosate (its slight degree of solubility prevents polariscopic examination), has a m. p. of about 162° . The author describes as d-caryophyllene nitrosate a nitrosate which he obtained from the blue caryophyllene nitrosite by treating it with boiling ligroin or by oxidation with chromic acid: m. p. 131 to 132° , $[\alpha]_D + 60^\circ$. From the blue nitrosite, m. p. 115° , β -caryophyllene nitrolbenzylamine (m. p. 172 to 173°) may be prepared; hence the active hydrocarbon of "caryophyllene", which Deussen calls β -caryophyllene, must be the base of this nitrosite.

¹⁾ Wallach, *Terpene und Campher*, Leipzig, 1909, p. 467. Report April 1907, 133; October 1907, 142; April 1908, 181; November 1908, 174; October 1909, 175.

²⁾ Comp. Report April 1909, 122.

³⁾ Report April 1908, 182; November 1908, 176; April 1909, 124.

⁴⁾ Liebigs Annalen 369 (1909), 41.

Together with this β -caryophyllene occurs a likewise lævorotatory hydrocarbon, to which Deussen assigns the name γ -caryophyllene. The blue nitrosite he calls β -caryophyllene nitrosite; the colourless nitrosite with a m. p. of 139° which is derived from the latter by a short treatment with alcoholic potash: β -caryophyllene isonitrosite. By exposing the blue nitrosite to the action of light while in alcoholic solution the above-mentioned d-caryophyllene nitrosate, m. p. 131° to 132° , (113 to 114° according to Schreiner and Kremers) is obtained while in benzene solution it yields a compound with m. p. 158 to 159° . When hydrochloric acid is split off from α -caryophyllene nitrosochloride with sodium methylate there is formed an inactive compound $C_{15}H_{25}NO_2$ (m. p. 116°); on the other hand, the action of sodium ethylate or propylate yields a body $C_{15}H_{23}NO$ melting between 128 and 129° . As is well known, the hydrocarbon which can be isolated from the mother liquor in the course of preparing the blue nitrosite¹⁾ yields two nitrosochlorides, one melting at 122° , the other at 146° . Singularly enough, these nitrosochlorides, as well as the β -caryophyllene nitrosochloride, when reacted upon with benzylamine, yield the identical β -caryophyllene nitrolbenzylamine, m. p. 172 to 173° . Deussen designates the nitrosochloride melting at 122° " α ", and that melting at 146° β -isocaryophyllene nitrosochloride. When isocaryophyllene is oxidised with dilute aqueous permanganate solution, the principal resultant product is the ketonic acid or aldehydic acid $C_{10}H_{16}O_3$ (m. p. of the semicarbazone 186°)²⁾, which has already been obtained on previous occasions. In addition there is formed a glycol, $C_{15}H_{24}O_2$ (m. p. 120° and α, α' -dimethyl succinic acid. Particulars concerning the various combinations are contained in A. Klemm's dissertation³⁾.

Styrene is known to possess the property of becoming converted when kept for a long time, especially at a warm temperature, into a polymeric compound, metastyrene, which has the appearance of a glassy amorphous mass. Until recently very little was known of the nature of this compound, but lately H. Stobbe and G. Posnjak⁴⁾ have been investigating the changes which styrene undergoes by the action of light and heat and have discovered that all the bodies which have hitherto been regarded as metastyrene are really mixtures of styrene and metastyrene or the reverse. They have prepared pure metastyrene by precipitating

¹⁾ Comp. Report November 1908, 176.

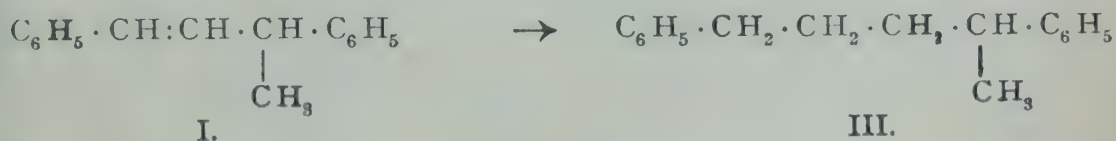
²⁾ Comp. Report April 1909, 124.

³⁾ Inaugural dissertation *Zur Kenntnis des Caryophyllens* of which a copy has been kindly sent to us by the author. This essay also contains a description of an apparatus for the ready preparation of nitrosochlorides of the mono- and sesquiterpenes, which, for the rest, is also referred to in Deussen's paper.

⁴⁾ Liebigs Annalen 371 (1910), 259.

the benzene-solution of the compound with alcohol. After repeating this process several times they obtained metastyrene in the form of a white, odourless, colloid body, fairly readily soluble in the aromatic hydrocarbons as well as in carbon tetrachloride and nitrobenzene. The authors have also cleared up the problem of the rate of velocity at which metastyrene is formed. This they succeeded in doing by determining the viscosity, basing their process upon the fact that the internal friction of the solution increases proportionately to the quantity of metastyrene dissolved. The measurements were conducted with styrene in which polymerisation had been setup partly by heating, and partly by the ultra-violet rays of a quartz lamp. It was shown that the process of polymerisation progressed more rapidly in the later than in the initial stages. They also found that when styrene had once been exposed to the light it afterwards continued to polymerise in the dark.

The same authors¹⁾ have determined the constitution of the liquid and solid di-styrene which is obtained by heating cinnamic acid with hydrobromic acid²⁾ or with 50 per cent. sulphuric acid³⁾, or again, by the dry distillation of cinnamate and acetate of lime⁴⁾. They regard the liquid body as α, γ -diphenyl- α, β -butene (I), and the solid as α, δ -diphenyl- α, β -butene (II), arriving at this conclusion from the oxidation- and reduction-products of the dibromides. When oxidised, the two di-styrenes yield benzoic acid and benzaldehyde; when reduced the dibromide of the liquid di-styrene yields α, γ -diphenyl-butane (III), and the dibromide of the solide di-styrene, α, δ -diphenyl-butane (IV).



Further proof of the structural isomerism of the two styrenes was afforded by the determination of the absorptionspectra, which differed from each other.

Di-styrene must not be regarded as an intermediate product of the styrene $\rightarrow$ meta-styrene reaction; for in none of the products of the various stages of the polymerisation of styrene could di-styrene be detected by the authors.

¹⁾ Ibid. 287.

²⁾ Erlenmeyer, Liebigs Annalen **135** (1865), 122.

³⁾ Fittig and E. Erdmann, Ibid. **216** (1883), 187.

⁴⁾ Engler and Leist, Berl. Berichte **6** (1873), 256.

Alcohols.

Linalool. Up to the present no uniform reaction-product had been obtained when hydrochloric acid gas was allowed to act upon linalool¹⁾ or geraniol²⁾. The reason of this, according to J. Dupont and L. Labaune³⁾, is that the investigators who have tried this reaction have omitted to use a solvent, and have failed to consider the temperature at which the reaction takes place. When hydrogen chloride gas is passed through linalool which has been diluted with its own weight of dry toluene and heated to 100°, water is split off and the hydrochloric ester of linalool, linalyl chloride, $C_{10}H_{17}Cl$, is obtained to the extent of 80%. Singularly enough, geraniol, when treated in the same manner, likewise yields linalyl chloride, although not so abundantly (about 60%). This compound possesses the following constants: b. p. 95 to 96° (6 mm.), d_{20}° 0,9341, $[\alpha]_{D20}^{\circ}$ + 1,50°, n_{D20}° 1,4813, mol. refr. found 52,5, calcul. 52,28. In order to regenerate at the alcohol the authors diluted the alcoholic solution of the chloride with nitrate of silver, when an almost inactive linalool was regenerated. By this method, therefore, starting from geraniol, they arrived at linalool, a conversion which had already been pointed out by Tiemann and Semmler⁴⁾, and which may also be accomplished by heating with water in an autoclave⁵⁾. The use of hydrochloric acid by the cold process gives less favourable results, for apparently a monochloride is formed which is contaminated with dichloride.

Cinnamic Alcohol. Dupont and Labaune⁶⁾, by following the process described under linalool (see above), and passing hydrogen chloride gas into a solution of cinnamic alcohol in toluene which had been warmed on the water-bath, have obtained 70% of cinnamyl chloride, b. p. 115 to 116° (6 mm.), d_{22}° 1,0857, n_{D22}° 1,583, mol. refr. found 46,79, calc. 46,94, m. p. of the dibromide 104°.

Conversion with nitrate of silver resulted in a mixture of two compounds boiling respectively at 88 to 89° (8 mm.) and 108° (8 mm.), as to the nature of which Dupont and Labaune are still unable to

¹⁾ Comp. Grosser, Berl. Berichte 14 (1881), 2494; Barbier, Compt. rend. 114 (1892), 674; Morin, Compt. rend. 92 (1881), 999; 94 (1882), 733; Bertram und Walbaum, Journ. f. prakt. Chem. II. 45 (1892), 597; Barbier, Bull. Soc. chim. III. 9 (1893), 915.

²⁾ Jacobsen, Liebigs Annalen 157 (1871), 915; Barbier and Bouveault, Bull. Soc. chim. III. 15 (1896), 594; Reyckler, ibid. 364; Tiemann and Semmler, Berl. Berichte 31 (1898), 832; Report October 1898, 54.

³⁾ Berichte of Roure-Bertrand Fils, October 1909, 21.

⁴⁾ loc. cit.

⁵⁾ Report April 1898, 27.

⁶⁾ Berichte of Roure-Bertrand Fils, October 1909, 34.

make any definite statements. They are of opinion that as yet it is impossible to decide with certainty whether their cinnamyl chloride is identical with that described by Klages and Klenk¹⁾.

Shortly before the publication of the paper referred to above, H. Emde and M. Franke²⁾ had also taken up the investigation of cinnamyl chloride ("styryl chloride") which, unlike Dupont and Labaune, they prepared at 0°, by passing dry hydrochloric acid over crystallised cinnamic alcohol until the weight of alcohol had increased from 34 to 100 g. After having been washed out with water, the chloride was distilled *in vacuo* (b. p. 140° [37 mm.]; 115° [13 mm.]), for further purification, but in the course of this operation hydrochloric acid was split off and the chloride was partly decomposed. By reciprocal action with aliphatic and cyclic amines a series of derivatives was obtained, of most of which the platinum and gold double-salts were also prepared.

As there is no mention in chemical literature of any derivatives which lend themselves to the rapid identification of cinnamic alcohol, we have prepared the phenyl- and diphenyl-urethanes of that body by the familiar method. The phenyl urethane crystallises out from petroleum ether in downy needles and from carbon tetrachloride or dilute alcohol in flat prisms, m. p. 90 to 91,5°. But the diphenyl urethane, which crystallises out from dilute alcohol in prisms (m. p. 97 to 98°) is still better adapted for the identification of cinnamic alcohol because of its well defined m. p. A combustion of the two derivatives gave the following values: —

Phenylurethane: 0,1492 g. subst.: 0,4143 g. CO₂, 0,0842 g. H₂O.

Found		Calc. for C ₁₆ H ₁₅ O ₂ N	
C	75,73%		75,89%
H	6,27%		5,93%

Diphenylurethane: 0,1461 g. subst.: 0,4292 g. CO₂, 0,0865 g. H₂O.

Found		Calc. for C ₂₂ H ₁₉ O ₂ N	
C	80,11%		80,23%
H	6,58%		6,66%

Aldehydes.

Methoxysalicylic aldehyde. A short time ago we reported on an aldehyde which had been discovered by Goulding and Pelly³⁾ in the root of a variety of *Chlorocodon* (*Whitei*?) but of which the authors had been unable to ascertain the constitution. Recently P. Friedländer⁴⁾ has

¹⁾ Berl. Berichte 39 (1906), 2552.

²⁾ Arch. der Pharm. 247 (1909), 333.

³⁾ Proceed. chem. Soc. 24 (1908), 62; Report November 1908, 196.

⁴⁾ Monatsh. f. Chem. 30 (1909), 879.

found that this compound is p-methoxysalicylic aldehyde, a body which had already been obtained many years ago by Tiemann and Parrisius¹⁾ by acting with chloroform upon a highly alkaline solution of monomethyl-resorcinol, as well as by the methylation of resorcinic aldehyde (2, 4-dihydroxy benzaldehyde). Friedländer and Schuloff have lately²⁾ observed the formation of this aldehyde when splitting up 4-methoxybenzene-2-indolindigo (from resorcinol monomethylether and isatine-chloride).

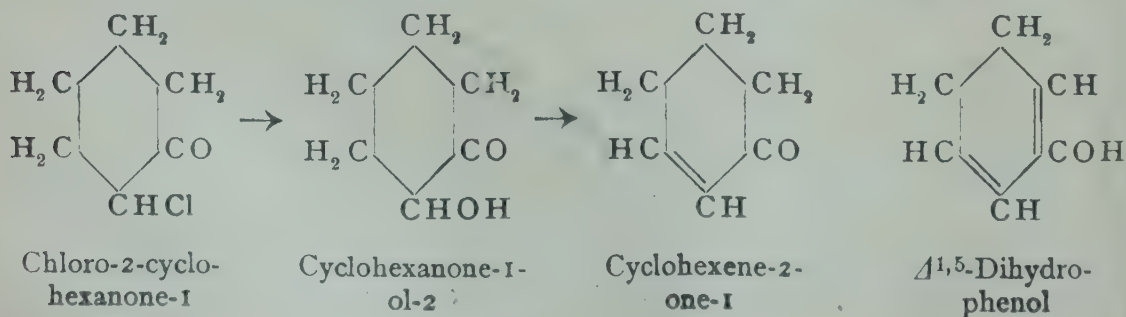
The most suitable way of preparing the compound is by the method of Tiemann and Parrisius, slightly modified. Resorcinic aldehyde and dimethyl sulphate are dissolved in a small quantity of methyl alcohol and rendered alkaline under heating by the addition of concentrated sodium carbonate solution. p-Methoxysalicylic aldehyde is formed almost at once and may be purified by distillation with steam. That this body is identical with the aldehyde from methoxybenzene indolindigo and with that from *Chlorocodon*-root is proved by the melting points of the aldehyde, the hydrazone and the oxime: —

Melting points:

	from <i>Chlorocodon</i> oil	Synthetic product
Aldehyde . . .	41 to 42°	41°
Hydrazone . . .	137 to 138°	138°
Oxime	138°	138°

Ketones.

A. Kötz³⁾, in collaboration with Th. Grethe, has published a paper on α, β -cyclohexenone, (cyclohexenone-2-one-1, $\Delta^{1,5}$ -dihydrophenol), a compound which is of interest because of the grouping of its atoms $\text{CH}=\text{CH}\cdot\text{C}=\text{O}$, a conjugated system of two dissimilar double-linkings. By acting with chlorine upon cyclohexanone, chloro-2-cyclohexanone-1 was obtained, which yielded cyclohexanone-1-ol-2, when heated with concentrated solution of potassium carbonate.



¹⁾ Berl. Berichte **13** (1880), 2366.

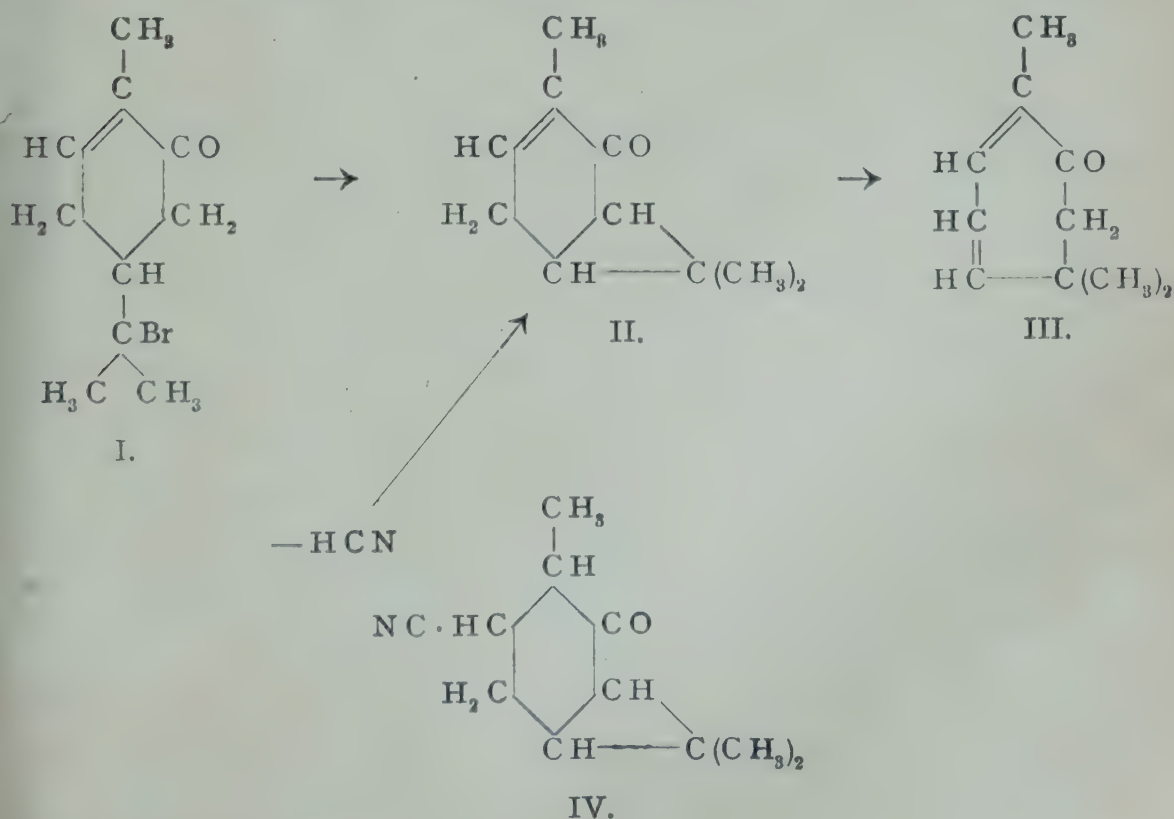
²⁾ Monatsh. f. Chem. **29** (1908), 387.

³⁾ Journ. f. prakt. Chem. II. **80** (1909), 473.

By warming this body with anhydrous oxalic acid, water was split off, and cyclohexene-2-one-1 (α, β -cyclohexenone) was obtained. This is an oil of aromatic odour, possessing the following properties: b. p. 63° (14 mm.), $d_{18^\circ} 0.9868$, $n_{D18^\circ} 1.4796$. Its semicarbazone melts at 161° , its oxime at 75 to 76° (from hot water). α, β -cyclohexenone may also be obtained from cyclohexanone-1-xanthogenic acid methylester-2 by dry distillation, or from bromo-2-cyclohexanone-1 by heating with anhydrous sodium acetate and glacial acetic acid, or with aniline. It is obtainable by similar means from chloro-2-cyclohexanone-1. When carbon dioxide is allowed to react upon a solution of α, β -cyclohexenone in ether, in the presence of sodium, the resultant compound is cyclohexene-3-one-2-carboxylic acid-1 or $\Delta^{1,3}$ -dihydrosalicylic acid, of which the ethyl ester forms a yellow oil of intense, aromatic odour, which boils at 115 to 117° (15 mm.).

The same ester is obtainable from α, β -cyclohexenone by condensing with oxalic ester and sodium ethylate. With benzaldehyde, α, β -cyclohexenone condenses into a benzal compound $C_{18}H_{12}O$, a yellow-coloured oil; b. p. 172 to 175° (15 mm.). The authors state that they are continuing their investigations.

Carvone. In a previous Report we stated that Wallach¹⁾ believes the formation of eucarvone (III) from the hydrobromide of



¹⁾ Liebigs Annalen 339 (1905), 94; Report October 1905, 113.

carvone (I) to proceed in the following manner: — An intermediate body (II), of a constitution analogous to carone is formed from which, by disruption of the tricyclic ring, eucarvone (III) results. Clarke and Lapworth¹⁾ have attempted to isolate this intermediate compound by splitting off hydrocyanic acid from cyanocarone (IV) but on doing this they obtained, instead of the compound looked for eucarvone.

In the preparation of cyanocarone the authors started from cyano dihydrocarvone dihydrobromide²⁾, from which, by treating it with methyl-alcoholic potash, they split off hydrogen cyanide by the cold method. The cyanocarone recrystallised from alcohol occurs in large, hexagonal, colourless, transparent crystals, m. p. 54 to 55°, sp. rot. $[\alpha]_D + 298^\circ$ (0,201 g. to 25,05 cc. of alcoholic solution). The semicarbazone melts, not very clearly, at 218 to 221° with slight decomposition. The hydrocyanic acid was split off from the cyanocarone by heating the latter with aqueous sodium hydroxide in the presence of ferrous hydroxide, in the course of which process, as already stated above, eucarvone was formed. The conversion does not take place quantitatively, but a considerable proportion of a compound $C_{11}H_{17}O_2N$, m. p. 210 to 212°, is formed. The constitution of this was not ascertained. When cyanocarone is heated on the water bath with concentrated hydrochloric acid, the result is a mixture of the stereoisomeric dihydrocarvone-carboxylic acids; when a mixture of cyanocarone and concentrated hydrochloric acid is saturated with hydrogen chloride gas by the cold method, cyano-dihydrocarvone hydrochloride, m. p. 69° (from alcohol), $[\alpha]_{D18} + 25,3^\circ$ (0,402 subst. to 25 cc. alcoholic solution) is formed. Upon being dissolved in glacial acetic-hydrobromic acid, cyanocarone yields cyano dihydrocarvone hydrobromide, m. p. 85°, $[\alpha]_{D14} + 25,5^\circ$ (0,3546 subst. to 25,1 cc. of alcoholic solution). When cyanocarone is left in prolonged contact with concentrated hydrochloric acid, the result, after the liquid has been rendered alkaline, is an amide, m. p. 130°, $[\alpha]_{D18,5} + 71,2^\circ$ (0,2335 g. subst. to 25 cc. of alcoholic solution), which is most probably isomeric with the previously described amide of dihydrocarvone-carboxylic acid³⁾. Oxidation of cyanocarone with a 4% aqueous solution of permanganate of potassium results in *cis*-caronic acid, a compound which has been prepared from carone by Baeyer and Ipatieff⁴⁾ synthetically by Perkin and Thorpe⁵⁾.

¹⁾ Journ. chem. Soc. 97 (1910), 11.

²⁾ Lapworth, Journ. chem. Soc. 89 (1906), 1826; Comp. Report April 1907, 152.

³⁾ Journ. chem. Soc. 89 (1906), 958.

⁴⁾ Berl. Berichte 29 (1896), 2796.

⁵⁾ Journ. chem. Soc. 75 (1899), 48.

In our previous Report¹⁾ we stated that Deussen, by acting with sodium methylate upon d-limonene nitrosochloride, had obtained a derivative which he called β -carvoxime. In the meantime, Deussen, in conjunction with Hahn²⁾, has continued the examination of this body. They found that d- β -carvoxime can be obtained both from d- α and from d- β -limonene nitrosochloride, and they also, from l-limonene nitrosochloride, prepared l- β -carvoxime (m. p. 56 to 57°; m. p. of the benzoic ester 76 to 77°). A mixture of equal parts of d- and l- α -carvoxime benzoate melts at 55 to 56°. Starting from the idea that, by heating d-limonene- α -nitrolaniline they would obtain l- α -carvoxime; and by similarly treating d-limonene- β -nitrolaniline, d- β -carvoxime, the authors heated both nitrolanilines to 140°, but in each case they obtained l- α -carvoxime.

A brief mention is also made of a few experiments which are described in detail in a dissertation by A. Hahn³⁾. Among these experiments were the heating of an alcoholic solution of l- α -carvoxime in a reflux-condenser, in the course of which it is rendered partly inactive; the preparation of L- and D-d-tetrabromo- α -carvoxime benzoic ester, m. p. 135 to 136°, $[\alpha]_D + 25,97$ and $- 25,51^\circ$ respectively, and the discovery of an oximido-group in the limonene-nitrolanilines.

Camphor. Hitherto no way has been known of splitting-up synthetic camphor into its optically-active component parts. Rewald⁴⁾ has succeeded in dismembering racemic camphor-sulpho-acid, (which can be prepared from the racemic compound by Reychler's method) into its optical antipodes by fractional crystallisation of the brucine salts. The salt of the dextrorotatory acid was the more sparingly soluble of the two, and was obtainable in an almost pure state, while the more readily soluble lævogyrate salt yielded a somewhat less pure acid. This was ascertained by comparing the rotation of the two acids with the constants determined by Reychler in pure samples.

By treating camphor with iodide of mercury in the presence of alcoholic or aqueous potash, either with or without iodide of potassium, Marsh and de Jersey Fleming Struthers⁵⁾ obtained iodo-mercuric substitution products of camphor of varying constitution. Cold solutions of alcoholic potassium alcoholate and aqueous potassium hydrate yielded a

¹⁾ Report October 1909, 190.

²⁾ Berl. Berichte 43 (1910), 519.

³⁾ *Beiträge zur Kenntnis der Mono- und Sesquiterpene* (Leipzig 1910), of which a copy was kindly sent to us by the author.

⁴⁾ Berl. Berichte 42 (1909), 3136.

⁵⁾ Journ. chem. Soc. 95 (1909), 1777; comp. Report April 1908, 189.

compound called dimercuric camphor-diiodide ($C_{10}H_{14}OHg_2I_2$). Ho aqueous liquor, in the presence of excess of iodide of potassium resulted in tetrameric tricamphor-diiodide $(C_{10}H_{14}O)_3Hg_4I_2$. When excess of iodide of potassium was avoided, the result was a compound $(C_{10}H_{14}O)_4Hg_5I_2$, and when the quantity of iodide of potassium used was insufficient, a body $(C_{10}H_{14}O)_5Hg_6I_2$ was formed. By successively acting upon the first-named of these compounds with acetic acid and halogen-alkalies, bodies were obtained with the formula $C_{10}H_{15}OHg \cdot X$ ($X = \text{halogen}$) to which an oxide corresponded which was obtainable by a different method. It was further discovered that when the aqueous solution is shaken with formic or acetic ester the double salt K_2HgI_4 which is soluble in water, decomposes according to the equation $3K_2HgI_4 = 2KHgI_3 + (KI)_4HgI_2$, the first-named double salt being taken up in the ester, the latter remaining in solution in the water. Analogous to this process an oil separates out in drops on the surface which before long congeals in pale yellow hard crystals. These possess the formula $KHgI_3 \cdot 4C_{10}H_{16}O$ and melt at about 65° when an alcoholic camphor solution is shaken up with a solution of iodide of mercury in aqueous iodide of potassium.

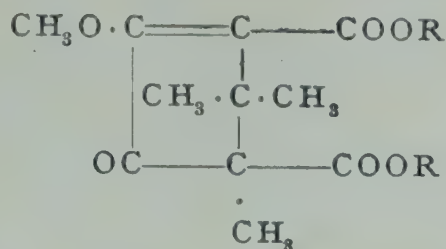
It is a commonplace that the history of the investigation of camphoric acid and its congeners is closely allied with that of camphor itself. Komppa¹⁾ who, many years ago, was the first to achieve the successful synthesis of apocamphoric and camphoric acids as well as of camphor itself, has now published two detailed papers in which he gives an account of the wearisome efforts (the initial stages of which go back more than 15 years), to synthesise in the first place apocamphoric acid. These experiments must be looked upon, in a sense, as the preliminaries to the synthesis of camphoric acid, concerning which we have already reported on a previous occasion in connection with a preliminary publication by the same author²⁾. The papers now under review, which may be considered as putting an end to the doubts raised by Blanc³⁾ as to the possibility of the synthesis are, broadly speaking, an exposition, furnished with full theoretical and experimental details, of a synthesis of which the outlines were already known. In addition, Komppa now gives the results of his investigation of certain by-products of the camphoric acid synthesis. These by-products, which had not been considered in detail in the original publication, are the non-anhydriable acid which has been identified as racemic *isocamphoric* acid (m. p. 180° to 190°), and a body obtained in the process of methylating diketo

¹⁾ Liebig's Annalen 368 (1909), 110; 370 (1909), 209.

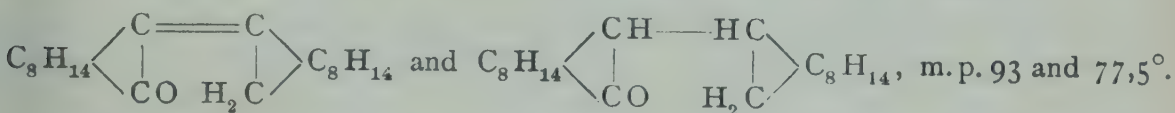
²⁾ Report April 1904, 98.

³⁾ Comp. Report October 1909, 198.

apocamphoric acid ester. Upon preliminary data this body is regarded as a doubly methylated ester of the ketone-enolic form: —



Guerbet¹⁾ has been subjecting to fractional distillation the oils which, in addition to camphoric acid, result from the reaction of sodium with camphor at 280°. He was, however, able to isolate solidifying substances only from the fractions which passed over between 326 and 335°, and the oxygen-content of these bodies was too high to entitle them to be regarded as derivatives of colophene, as they were originally supposed to be. By means of fractional crystallisation from alcohol Guerbet succeeded in obtaining two bodies, C₂₀H₃₀O and C₂₀H₃₂O to which, after continued investigations, he assigned respectively the formulae of a bornylene- and a bornyl-camphor: —



The first-named compound results from the action of sodium-camphor on the ketone group of a second molecule of camphor by splitting-off sodium hydroxide, and from this, by attachment of the hydrogen which is set free in the process of forming sodium-camphor, the second compound, bornyl camphor, is generated.

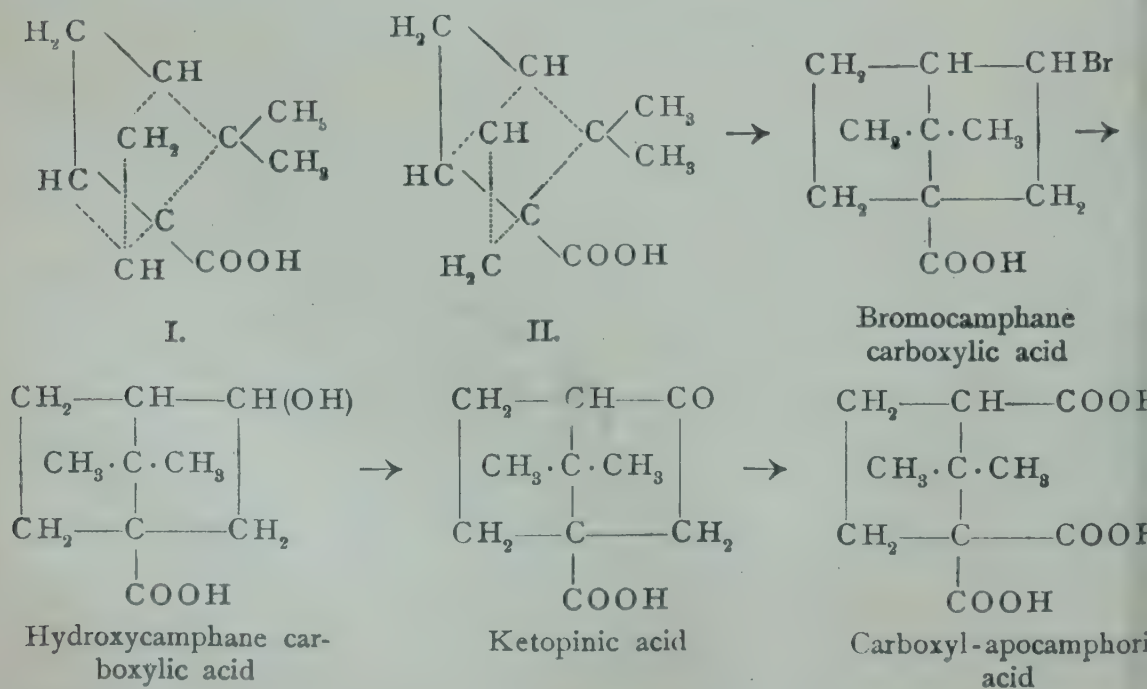
Some considerable time ago Wagner and Majewski, by splitting-off water from their hydroxycamphenilanic acid, obtained an acid C₁₀H₁₄O₂, which they described as dehydrocamphenilanic acid, and which even at that time was regarded as a tricyclic compound and termed later on tricyclene carboxylic acid. Subsequently this body was repeatedly prepared by Brecht and Jagelki²⁾ and by several other investigators. Recently, Brecht and May³⁾ have discovered a very ready method of preparing this acid. This method consists of introducing small quantities of camphenile nitrite (from camphene with nitrous acid), into ice-cold concentrated sulphuric acid. The solution, after having been left standing for some time, was poured on ice, the aqueous solution boiled, and finally subjected to steam-distillation. In this process the acid volatilised and was

¹⁾ Compt. rend. **149** (1909), 931; Bull. Soc. chim. IV. **7** (1910), 64.

²⁾ Comp. Report April 1900, 55.

³⁾ Chem. Ztg. **33** (1909), 1265.

recovered from the distillate to the extent of from 70 to 80% of the theoretical yield. In addition to the acid there were formed two likewise volatile, lactones, of which the composition has not been investigated more closely. These melted respectively at 198 and 137° and further particulars concerning them will probably to be published elsewhere. The manner by which the structure of tricyclene carboxylic acid¹⁾ was ascertained consisted in attaching HBr to one of the ring-linkings by immersing the body into aqueous fuming hydrobromic acid. The resultant acid, known as bromo-apocamphane carboxylic acid (m. p. 195° under liberation of hydrobromic acid) could be converted by reduction with zinc-dust and glacial acetic acid into the corresponding bromine-free acid (m. p. 218°). Boiling with excess of soda solution converted the brominated acid to the extent of 81% into the sodium salt of the corresponding hydroxy-acid (m. p. 237°) and the dry distillation of the last-named yielded, in addition to regenerated tricyclene carboxylic acid, two lactones, with m. p. 137 to 138° and 145 to 147° respectively. Oxidation of the sodium salt of hydroxycamphane carboxylic acid with neutral solution of permanganate resulted in a yield of 82% of ketopininc acid, m. p. 234°, from which, by the well-known method with nitric acid, carboxyl-apocamphoric acid and, further, apocamphoric acid were obtainable. This process of reaction induced Bredt and May to suggest formula II in lieu of Semmler's formula I for tricyclene carboxylic acid with a tricyclic ring. This formula II obviates Semmler's necessity of assuming a bornylene-like conversion-product and explains in the manner subjoined, the formation of the conversion-products referred to above:



¹⁾ Chem. Ztg. 34 (1910), 65.

Fenchone. A few years ago Semmler¹⁾ maintained that fenchone was not decomposed by sodium, and suggested that this peculiarity should be made use of for separating this ketone from camphor. The most recent researches of Wallach²⁾, however, show that Semmler's assertion was incorrect, and that sodium does in effect react with fenchone, although not so rapidly as with camphor. Hence the semicarbazide method³⁾ which was recommended by Wallach some time ago³⁾ remains the only accurate one; the sodium-process involving, furthermore, a considerable loss of fenchone.

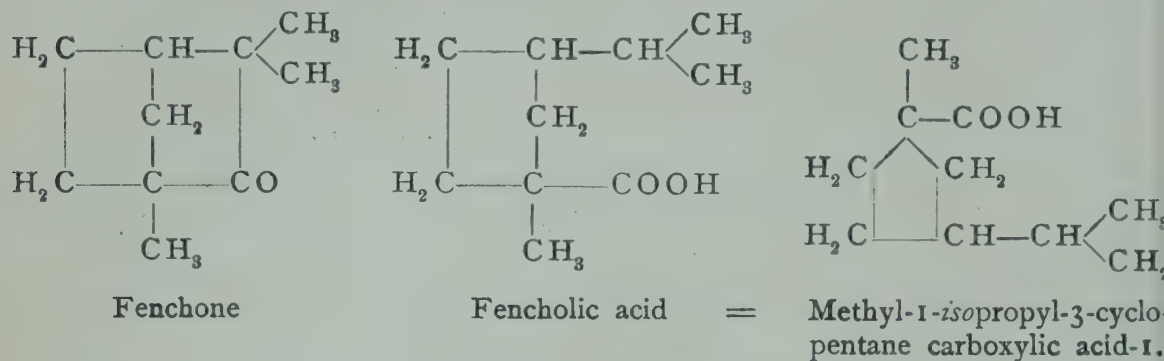
If fenchone, after having been previously diluted with toluene, is heated for 8 hours with a reflux-condenser in a hydrogen current with one molecule of sodium, fenchyl alcohol and the pinacone of fenchone are formed as neutral products of reaction. The pinacone occurs in prisms or in thick slabs, m. p. 97° ; b. p. 360 to 365° (with slight decomposition); 219 to 220° (13 mm.); $[\alpha]_D +45,00^{\circ}$ (in acetic ester), $-44,78^{\circ}$ (in acetic ester) or $-36,70^{\circ}$ (in benzene). The racemic mixture melts at 104 to 105° . The reaction proceeds much more easily and quickly, however, if potassium is employed instead of sodium. A volatile acid was also observed, and as it was naturally inferred that this acid was due to the formation of caustic soda (in analogy with the formation of campholic acid from camphor and sodium hydroxide), 2 parts of fenchone were heated in an autoclave for 24 hours with 3 to 4 parts of potassium hydroxide up to 220 to 240° . This process resulted in an almost quantitative yield of an acid volatilising with steam and possessing the following properties: m. p. 18 to 19° , b. p. 255 to 256° (normal press.), 151 to 152° (17 mm.), $d_{20} 0,9700$, $n_{D20} 1,4563$. Judging by its composition ($C_{10}H_{18}O_2$) and the manner of its formation, this acid is altogether analogous with campholic acid; for which reason Wallach has provisionally called it fencholic acid. It is combined with a small proportion of an isomeric acid which has not been more closely investigated. Fencholic acid is a weak acid, which is precipitated from the solution of its alkaline salts by excess of carbon dioxide gas. It is noteworthy that the alkaline salts and certain other salts are partly volatilisable without decomposition. For purposes of identification a series of derivatives were prepared, viz., fencholic acid chloride: b. p. 218 to 219° (750 mm.), 100° (15 mm.), $d_{20} 1,0045$, $[\alpha]_{D19} -2,43^{\circ}$, $n_{D20} 1,4606$; ethyl ester of fencholic acid: b. p. 222 to 223° , $d_{19} 0,913$, $n_{D19} 1,4392$; isomeric ester of fencholic acid: b. p. 262 to 269° , $d_{19} 0,903$, $n_{D19} 1,4436$; fencholic acid amide: m. p. 94° , and fencholic acid anilide: m. p. 79

¹⁾ Berl. Berichte **40** (1907), 4591; Report April 1908, 189.

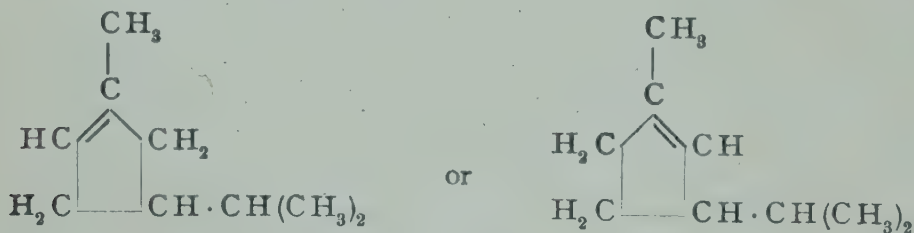
²⁾ Liebigs Annalen **369** (1909), 63.

³⁾ Liebigs Annalen **353** (1907), 209; Report October 1907, 159.

to 80° . Fencholic acid is identical with dihydro-fencholenic acid-b, which Semmler¹⁾ had already previously prepared by saponifying the amide which he had obtained by treating fenchone with sodium amide. The subjoined formula shows the generation of fencholic acid (which is probably to be regarded as being methyl-1-isopropyl-3-cyclopentane carboxylic acid-1):



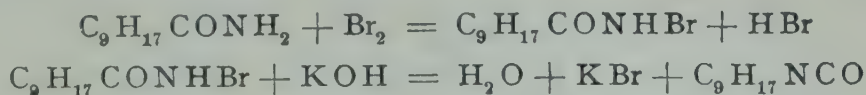
When fencholate of sodium is subjected to dry distillation the last portion which passes over is an unsaturated hydrocarbon, C_9H_{16} which may be prepared more readily and in purer form by distillation from fenchylamine hydrochloride (see below) and which possesses one of the two following formulæ: —



Its constants are as follow: b. p. 142 to 143° , $d_{21}^{\circ} 0.7945$, $[\alpha]_D + 66.21^{\circ}$, $n_{D21}^{\circ} 1.4403$. The nitrosochloride ($\text{C}_9\text{H}_{16}\text{NOCl}$)₂ which is apparently not uniform, melts at 115° (from acetone); the nitropiperidine at 158 to 159° . The nitrosochloride was obtained both in the solid and in the liquid form. The solid nitrosochloride yielded under elimination of hydrochloric acid the oxime of an unsaturated ketone $\text{C}_9\text{H}_{14}\text{O}$ which had a well-defined odour of carvone boiled at 204 to 206° , and gave a semicarbazone melting at 149 to 150° . When Hofmann's reaction is applied to fencholic acid amide (dihydrofencholene amide) there is formed, according to the statements of Bouveault and Levallois²⁾, an urea ($\text{C}_9\text{H}_{17}\text{NH}$)₂CO, m. p. 168 to 169° . But this statement is not altogether correct, for Wallach has found that the ultimate products of reaction of fencholyl amide with bromine and potash liquor depend wholly upon the conditions under

¹⁾ Berl. Berichte **39** (1906), 2578; Report October **1906**, 137.
²⁾ Compt. rend. **146** (1908), 180; Report April **1908**, 189.

which the experiment is conducted. If the quantitative proportions indicated in the following equations:



are accurately adhered to, the result is fenchelylisocyanate, $\text{C}_9\text{H}_{17}\text{NCO}$, a liquid of a faint yellow colour, volatilising with steam and possessing a slight, not unpleasant odour. This body has the following constants: b. p. 201° , $d_{19^\circ} 0.9210$, $[\alpha]_{\text{D}19^\circ} + 3.04^\circ$, $n_{\text{D}19^\circ} 1.4461$. On treatment with bases, the result was the corresponding urea $\text{C}_9\text{H}_{17}\text{NHCONH}_2$ m. p. 129 to 130° . When treated with mineral acids the cyanate is split up quantitatively into carbon dioxide and fenchelylamine $\text{C}_9\text{H}_{17}\text{NH}_2$, a very mobile liquid possessing the following properties: b. p. 173° , $d_{21^\circ} 0.832$, $\alpha_{\text{D}} \pm 0$, $n_{\text{D}21^\circ} 1.4450$. The hydrochloride melts at 169 to 170° and, when subjected to dry distillation, yields the hydrocarbon referred to above.

If fencholenic acid is oxidised with an aqueous solution of permanganate of potassium the principal resultant products are two non-volatile isomeric mono-hydroxyfencholic and two isomeric dihydroxy-fencholic acids. Under the influence of mineral acids the mono-hydroxyfencholic acids yield volatile lactones and the dihydroxyfencholic acids non-volatile hydroxylactones. There is also formed a slight proportion of a lactone $\text{C}_{10}\text{H}_{16}\text{O}_2$ which volatilises with steam. The observations recorded above cannot be explained by Wallach's fenchone formula, but they can be so explained by Semmler's formula, the justification of which, as stated by Semmler, he (Wallach) does not, however, altogether acknowledge. Wallach approves, though, of the latter's formula on the ground of the acid derivatives from fenchone which are described above, and of which he is the discoverer.

Upon heating *isofenchone* with potassium hydroxide under conditions similar to those stated above for fenchone, *isofencholic acid*, m. p. 33 to 34° , results. The amide melts at 65 to 66° , the anilide at 100 to 101° . Further examination of this acid is promised.

To the interesting question as to the behaviour of monocyclic ketones under hydrolytic decomposition with potassium hydroxide the unexpected answer is made that unsaturated fatty acids although in poor yield, and not as could be surmised formed, saturated fatty acids are. In this case the power of condensation of the simple cyclic ketones was strongly in evidence, neutral bodies being formed in the course of the process. For instance, cyclohexanone and caustic potash yielded bicyclohexane, a tricyclic hydrocarbon $\text{C}_{18}\text{H}_{24}$, a product of condensation $\text{C}_{18}\text{H}_{26}\text{O}$, and an acid $\text{C}_{12}\text{H}_{20}\text{O}_2$. A similar behaviour was displayed by the monomethylated cyclohexanones, neutral products and high-molecular acids being formed.

Leroide¹⁾ regards it as a disadvantage of the method proposed by Semmler, referred to above, for the separation of camphor and fenchone, that it is accompanied by the formation of fenchyl alcohol and borneol sodium, as a result of which the process must be repeated several times before it yields a pure product. The author himself has experimented with various methods for the preparation of a camphor free fenchone and has come to the following conclusions: — fractionated crystallisation is not successful; 1 kilo technically pure fenchone (m. p. $+6^{\circ}$) was recrystallised six times, but at the end of the experiment its composition had not undergone the slightest change. An attempt to expel the camphor by sublimation under slightly diminished pressure in a current of carbon dioxide gas was also fruitless, which is not surprising when it is remembered that camphor has a higher b. p. than fenchone. By the action of sodium ethylate pure fenchone may be produced, because camphor is much more readily attacked than fenchone, but only with considerable loss. Another method of purification which has been tried by Leroide is founded upon the action of bromine on a solution in ligroin, in which process camphor forms a substitution product, whereas fenchone gives an additive compound, which is easily decomposed by water. In order to carry out this separation, the fenchone, dissolved in chloroform, was warmed on the water bath with bromine, and after two hours the mass was first washed with pure water, and afterwards with water with an alkaline reaction. It was then dried and distilled. After repeating the process several times, a camphor-free product may be obtained, but the loss is fairly heavy, because in the end bromo-substituted fenchone is formed. A much better result can be achieved by treating fenchone with bromine in the presence of aluminium chloride. To 100 g. fenchone which are heated with 5 g. aluminium chloride in a reflux condenser, Leroide, very gradually, added 50 g. bromine. After two hours the mass was treated with water, as described above, and distilled, the result being a yield of 80% camphor-free fenchone. In order to explain the course of the reaction, Leroide assumes that camphor forms a molecular compound with aluminium chloride, which, when heated, yields a mixture of two ketones. These ketones readily absorb bromine and can therefore easily be separated from fenchone by distillation. Leroide continues: "If this hypothesis was correct, the aluminium chloride by itself should be able to detain the camphor". This is actually the case, for when fenchone was heated with the reagent mentioned, the latter dissolved, colouring the contents of the flask brown. The process of distillation left as residue a viscous mass, which gave with water an oily liquid with scarcely any

¹⁾ Berichte of Roure-Bertrand Fils, October 1909, 38.

odour of camphor. The yield of camphor-free fenchone was 80%. The rotation was $[\alpha]_{D17^\circ} + 58,70^\circ$, whereas Wallach gives $[\alpha]_{D18^\circ} + 59,30^\circ$ for pure fenchone. This slight discrepancy may perhaps be traced to the racemising action of the aluminium chloride. The process of reaction, we must confess, is not quite clear to us, unless the ketones which are originated in the camphor-aluminium-chloride reaction have either a much higher or a much lower b. p. than fenchone.

In order to test the degree of sensitiveness of his method, Leroide prepared a 7,83 per cent. solution of camphor in fenchone, which had a rotation of $+ 57,30^\circ$ in a 10 cm. tube, while the original rotation of the fenchone was $58,40^\circ$. After being treated once with chloride of aluminium, the product rotated $+ 57,52^\circ$, after a second treatment, $+ 58,20^\circ$, the latter rotation remaining when the process was repeated. With semicarbazide it was also impossible to detect even a trace of camphor.

In order to ascertain the minimum proportion of camphor which can be detected by the semicarbazide, Leroide treated solutions containing 0,01, 0,005 and 0,001 g. of this ketone with semicarbazide. The latter could only be detected in the solution with 0,01 g. camphor.

Attempts to separate l-fenchone from thujone (a fraction of oil from *Thuja occidentalis*) by means of aluminium chloride were unsuccessful, viscous mixtures being formed from which no l-fenchone could be isolated.

Phenols and Phenol Ethers.

Isosafrol. Eykman¹⁾, in connection with chavicol, first laid stress upon the possibility that, in the process of conversion of allyl-into propenyl-compounds, the latter may appear in two geometrically-isomeric forms, but the existence of two such isomerides has only recently been proved by Hoering and Baum²⁾ in connection with isosafrol. In a sample of commercial isosafrol supplied by our firm these investigators discovered by careful, frequently repeated fractionation, in addition to small proportions of unaltered safrol, and besides the well-known isosafrol, an isomeride of the latter, with a lower b. p. and less density. The separation of the two bodies was effected more satisfactorily, although with not less trouble, after repeated fractionation from a first-runnings in the technical preparation of isosafrol supplied by us (in which the new isomeride must be accumulated). The portions with low b. p. which consisted principally of safrol and of the new isomeride (termed α -isosafrol) were treated with picric acid

¹⁾ Berl. Berichte **22** (1889), 2746.

²⁾ Ibidem **42** (1909), 3076.

according to the method of Bruni and Tornani¹⁾, because it appeared impossible to effect exact separation by fractionation alone. It was then found that the picrate of the known isomeride described as β -isosaflol, remained almost entirely stable under steam distillation *in vacuo* at 55 to 60°, under 9 to 15 mm. pressure, while the picrate of α -isosaflol, when subjected to the same treatment, decomposed almost completely, and could be distilled off together with the remaining saflol. The separation of the latter was effected by Balbiano's²⁾ mercuric acetate method. The α -isosaflol which was finally obtained after repeated application of this process of purification, and which must be regarded as the purest preparation hitherto obtainable, possessed the following constants: b. p. 242,2 to 242,5° (760 mm.), 116,2 to 116,3° (13,5 mm.), $d_{18,5^\circ}$ 1,1073, $n_{D18,5^\circ}$ 1,56344, n_{D15° 1,56535. Its b. p. and refractive index, therefore, lie midway between those of saflol and of the ordinary β -isosaflol, while the density approaches that of saflol very closely. Externally the two isomerides differ only in their odour; chemically no differences could be traced, inasmuch as all the reactions which were applied (preparation of the dibromide, the α -ketone [propiopiperone], the glycol, and of isochavibetol) invariably yielded the same bodies from both compounds.

It should here be stated that the flask referred to in Hoering and Baum's paper (p. 3081, footnote 4) as "Stephan's flask", is in reality a slightly modified form of a flask which was constructed in our laboratory many years ago by H. Walbaum and K. Stephan.

When isosaflol is reduced with sodium and alcohol³⁾, or with hydrogen and nickel⁴⁾, dihydrosafrol and *m*-propylphenol are formed. Another method for preparing dihydrosafrol consists, according to Fournier⁵⁾, in shaking an ethereal solution of saflol and isosaflol in an atmosphere of hydrogen in the presence of platinum-black (see also "pinene", p. 166). Eugenol and isoeugenol were reduceable in the same way, and gave the same dihydrogenated body, which proved to be identical with the propylguajacol which has been prepared by Delange⁶⁾ from eugenol and isoeugenol by reducing them with hydrogen and nickel. The b. p. of this propylguajacol (dihydroeugenol) is 124 to 125° (15 mm.); the benzoate melts at 73°.

¹⁾ Chem. Zentralbl. 1904, II. 254; Report April 1905, 86.

²⁾ Berl. Berichte 36 (1903), 3575; 42 (1909), 1502; Report April 1904, 100; October 1909, 204.

³⁾ Ciamician and Silber, Berl. Berichte 23 (1890), 1162.

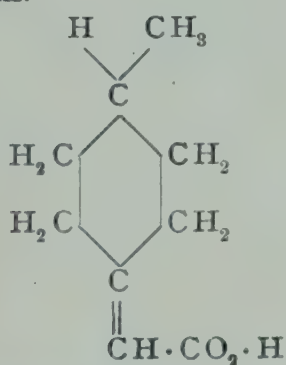
⁴⁾ Henrard, Chem. Weekblad 4 (1907), 630; Report April 1908, 195.

⁵⁾ Bull. Soc. chim. IV. 7 (1910), 23.

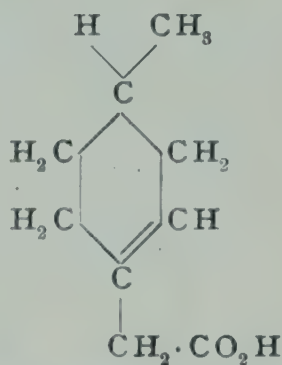
⁶⁾ Bull. Soc. chim. IV. 3 (1908), 505.

Acids.

In 1906, W. Marckwald, in conjunction with R. Meth¹⁾, described as 1-methylcyclohexylidene-4-acetic acid a compound which consisted of optically active components, notwithstanding the fact that the molecule contained no asymmetric carbon-atom. The possibility of the existence of such compounds had already been foreshadowed by Van't Hoff in his classical book on the grouping of the atoms in space. Shortly after the publication of Marckwald's paper, Perkin and Pope²⁾, announced that the acid in question was not 1-methylcyclohexylidene-4-acetic acid, but its isomeride, 1-methyl- Δ^3 -cyclohexene-4-acetic acid, a compound which actually does include an asymmetric carbon-atom.



1-Methylcyclohexylidene-4-acetic acid



1-Methyl- Δ^3 -cyclohexene-4-acetic acid

Recently, Perkin, Pope and Wallach³⁾, have succeeded in obtaining true methylcyclohexylidene acetic acid. In a publication which appears in their joint names they describe the splitting-up into its optical components of true 1-methylcyclohexylidene-4-acetic acid, which had been synthetically prepared by Wallach according to the bromo-acetic ester method. We refer to the original paper for the experimental details of the analysis, which was carried out by the aid of brucine-salts. The optical activity is based upon the fact that all symmetrical elements are wanting in the molecule of methylcyclohexylidene acetic acid, and that therefore the conditions are present for the setting up of enantiomorphic forms.

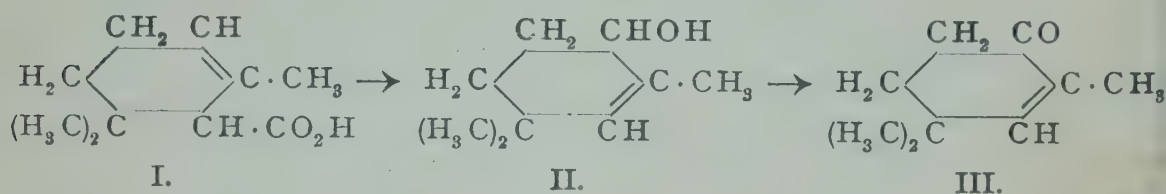
L-1-methylcyclohexylidene-4-acetic acid occurs in small colourless flaky crystals, possessing the following constants: m. p. 52,5 to 53°, $[\alpha]_D - 77,8$ to $- 81,1^\circ$ (in absolute alcohol), $- 74,6^\circ$ (in methylal), $- 74,4^\circ$ (in ether). d-1-methylcyclohexylidene-4-acetic acid: m. p. 52,5 to 53°, $[\alpha]_D + 78$ to $+ 81,4$ (in absolute alcohol) $+ 75,3^\circ$ (in methylal), $+ 75,3^\circ$ (in ether). The racemic mixture melts at 62,5 to 63°, but the original inactive compound at 66°.

¹⁾ Berl. Berichte **39** (1906), 1171.

²⁾ Proceed. chem. Soc. **22** (1906), 107; Journ. chem. Soc. **93** (1908), 1075.

³⁾ Journ. chem. Soc. **95** (1909), 1789; Liebigs Annalen **371** (1910), 180.

If α -cyclogeranic acid (I) is oxidised by means of hypoiodous acid (prepared by allowing iodine to react upon oxide of mercury in the presence of moist ether; or iodine upon aqueous solution of sodium carbonate), there results, according to J. Bougault¹), a ketone 1,5,5-trimethyl- Δ^6 -cyclohexenone-2 (III), which has already been described by Wallach²), but the principal compound produced is the corresponding alcohol 1,5,5-trimethyl- Δ^6 -cyclohexenol-2 (II). This presents itself in the form of a liquid with a camphoraceous odour, and with the following properties: b. p. 193° (760 mm.), $d_{40}^{19} 0,9310$, b. p. of the acetic ester 206 to 207° . By oxidising it with chromic acid mixture, trimethylcyclohexenone is obtained, which, however, cannot be reduced backwards into the alcohol in question, but yields instead trimethylcyclohexanol. Energetic oxidation of trimethylcyclohexenol results in acetic acid and α, α' -dimethyl glutaric acid.



Cinnamic acid. The investigation by C. Liebermann³) as to cinnamic acid, to which we referred in our previous Report, has been continued by this author in conjunction with H. Trucksäss⁴). On the basis of his experimental observations, which agree with the statements of Biilmann⁵) in all except a few details, Liebermann broadly confirms Biilmann's hypothesis of the trimorphy of *allo*-cinnamic acid and the two *isocinnamic* acids.

H. Stobbe⁶) has examined $1/10000$ normal alcoholic and aqueous solutions of the two *iso*-cinnamic acids, as well of *allo*-cinnamic acid, in a Steinheil quartz spectrometer and has found the absorption-spectra of the three acids to be in every respect identical, which points to the trimorphic character of *cis*-cinnamic acid.

In the meantime, Biilmann⁷) has also continued his investigations and has discovered that the solutions of the three acids possess a similar electrical conductivity, which again points to trimorphism. The conductivity was determined by N. Bjerrum with an Ostwald resistance-apparatus. Biilmann also discusses the atomic structure of cinnamic

¹) Compt. rend. **150** (1910), 397.

²) Liebigs Annalen **324** (1902), 97; comp. Report October **1902**, 87.

³) Berl. Berichte **42** (1909), 1027; Report October **1909**, 210.

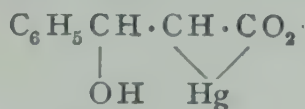
⁴) Berl. Berichte **42** (1909), 4659; **43** (1910), 411.

⁵) Comp. Report April **1909**, 140.

⁶) Berl. Berichte **43** (1910), 504.

⁷) Ibid. 568.

acids. He had already previously discovered that malenoidic acids, such as maleinic acid and citraconic acid give complex compounds when treated with mercuric salts, whereas fumaroidic acids, such as fumaric acid and mesaconic acid, do not react with such salts. From cinnamic acid with a m. p. of 133° no mercuric additive compound was obtained, while on the other hand the *allo*-acid gave a reaction resulting in the formation of α -mercuri- β -phenylhydracrylic acid,



thus showing that the *allo*-acid has a malenoidic structure. We refer to the original paper for the experimental details of this investigation.

C. N. Riiber and V. M. Goldschmidt¹⁾ have also occupied themselves with research into the conditions of isomerism of cinnamic acid. On the results of their examination they believe themselves warranted in concluding that Erlenmeyer's²⁾ synthetic cinnamic acid and α -heterocinnamic acid are in reality storacicacids which have been contaminated by substituted cinnamic acids. For instance, by mixing storax cinnamic acid with about 1% of chloro-cinnamic acid, they obtained a "synthetic" or α -heterocinnamic acid. An addition of 0.3% sufficed to convert storacic into synthetic cinnamic acid.

Nitrogenous Bodies.

We have already on a previous occasion³⁾ reported on the occurrence of skatol in the wood of *Celtis reticulosa* and of an African tree. C. A. Herter⁴⁾ has recently shown that the first-named wood contains not only skatol, but also indol. The skatol content is probably about 0.01%; singularly enough, the body was found only in the wood from the trunk, not in that of the branches, the bark, or the roots.

¹⁾ Berl. Berichte **43** (1910), 453.

²⁾ Comp. Report October 1909, 211.

³⁾ Report April 1903, 79.

⁴⁾ Journ. biol. Chem. **5** (1909), 489; according to Apotheker Ztg. **24** (1909), 885.

J. J. Weber, Leipzig.

SEMI-ANNUAL REPORT
OF
SCHIMMEL & Co.
(FRITZSCHE BROTHERS)

MILTITZ
NEAR LEIPZIG

LONDON * NEW YORK



OCTOBER 1911.

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List of abbreviations.

d = specific gravity.

$d_{20^{\circ}}$ = specific gravity at 20° , compared with water at 15° .

$d_{4^{\circ}}^{20^{\circ}}$ = specific gravity at 20° , compared with water at 4° .

$\alpha_{D20^{\circ}}$ = optical rotation at 20° , in a 100 mm. tube.

$[\alpha]_D$ = specific rotation.

$n_{D20^{\circ}}$ = index of refraction at 20° .

Sol. p. = solidifying point.

M. p. = melting point.

B. p. = boiling point.

n = normal.

Acid v. = acid value; ester v. = ester value; sap. v. = saponification value.

g. = gram; cc. cubic centimeter; mm. = millimeter.

Temperatures are uniformly given in degrees Centigrade.

The strength of alcohol, if not otherwise indicated, is given in per cent. by volume.

The course of business during the past half-year affords but slight occasion for detailed comment. In almost all branches, in which our manufactures are used, trade has been decidedly animated and healthy, and our expectations of a normal development of industry and commerce, as expressed in our last Report, have therefore been fulfilled in every respect. During the past summer our turnover has continued to show a very marked increase, and even the unprecedented tropical heat and drought, which have carried in their train such serious consequences for the whole economic life of the German nation, have not seriously affected the volume of our own trade. It goes without saying, however, that owing to the abnormal want of rain the crops of most of the raw materials which are employed in our industry have been failures, and that as a result we have to record considerable advances in price in almost all our oils, especially in those which are distilled from home-grown material, and of these advances particulars are given under the various headings of the present Report. The increase in the cost of food-stuffs which has been brought about by the abnormal climatic conditions, and the heavy burdens which are thereby laid upon the shoulders of the people, especially the working classes, are matters of serious concern for the whole of our German Industries, and the final results of the harvest in the principal corn-producing countries of the world are therefore awaited with grave anxiety.

In addition to these troubles there is the Morocco crisis. Within the past few weeks this has entered upon a stage which has given all Europe a political attack of nerves, — brought about chiefly by the unjustifiable mischief-making of the Jingo-press everywhere, — which may have incalculable consequences. The wildest rumours of a rupture of the negotiations were set afoot, and suddenly caused a veritable war-panic, which found expression in a downright slump on the Bourse such as had not been experienced for years, and, in certain towns, in a wild rush on the Savings-Banks. Unfortunately, at the moment when this Report goes to press, the negotiations have not yet reached a definite result, and we are therefore unable to comment upon their outcome, and to give a forecast of the further development of affairs. But there is scarcely

¹⁾ The Introduction to the present Report, as well as the Commercial part, were written in the month of September.

room for doubt that when the solution of this political question has been found (and it may be taken for granted that this solution will be a peaceful one), there will be a sigh of relief throughout commercial and industrial circles, for political uncertainty paralyses all business undertakings. But in spite of the fact that the political sky has not yet cleared, the money-market until quite recently remained easy. It is true that the bank-rate has risen, which is not surprising in view of the increasing demand for money, this being a standing feature of the Autumn-season, but it is pretty certain that there will be no further accentuation in the stringency of money, for the reason that the conditions described above have seriously impaired the spirit of industrial enterprise, so that it is hardly likely that there will be any exceptional demands upon the money-market from that quarter. That the development of Germany's foreign trade during the first eight months of the year 1911 has been highly satisfactory, is evident from the official export-figures given below: —

Value of German exports, Jan.—Aug. 1910: 4797,9 Million Marks

“ “ “ “ “ “ 1911: 5179,9 “ “

The value of German imports during the same period advanced from

5798,8 Million Marks in 1910, to

6157,6 “ “ “ 1911.

The quantitative figures of Germany's foreign trade in essential oils¹⁾ for the first seven months of the year are now available, and show the following result: —

Imports, January—July 1910: 712 300 kilos

“ “ “ 1911: 884 500 “

Exports, January—July 1910: 314 000 kilos

“ “ “ 1911: 342 400 “

The increase in the imports is again due to the growth in the imports of crude oils resulting from the favourable state of business.

The exports of artificial odoriferous compounds²⁾ also show a noteworthy increase. The figures were:

January—July 1910: 256 200 kilos

“ “ 1911: 283 300 “

Our branch-works at Bodenbach in Austria have been very busy indeed during the summer months, and in view of the steady increase in our commercial relations with the Austro-Hungarian Monarchy, we have felt that it was time to make suitable preparations to meet the growing demand upon our productive capacity by a large extension of our factory. This extension has been completed this summer and is already in working

¹⁾ No. 353 b/e Statistisches Warenverzeichnis.

²⁾ No. 354 b/e Statistisches Warenverzeichnis.

order. Generally speaking, business in the Austro-Hungarian market — a market to which we have become much attached owing to the intimate and long-standing connections we have established with it through our branch-house —, still suffers from many drawbacks, partly of a purely commercial, partly of a political character, to which we have not space to refer here. In the spirit and liqueur-industries in particular there are strong complaints of insecure prospects. Up to the present, the frequently-discussed increase in the spirit-tax has not yet been carried out so far as Austria is concerned, but in Hungary the tax has been raised to 1.40 Kronen per liter of pure alcohol. This advance, which was proposed in the Budget-Bill by the Minister of Finance and approved by the Chamber of Deputies, came into force on September 1st, and it is therefore of course impossible at present to form an opinion of the extent to which this new taxation will affect the trade in alcoholic preparations. The statistics show the foreign trade of Austria-Hungary to be in a condition of steady expansion. According to the Statistical Report of the Ministry of Commerce on the Foreign Trade of the Austro-Hungarian Customs-Union, the imports in the month of July of the present year showed a value of 245,4, and the exports a value of 195,3 million Kronen, representing increases of 36,4 and 4,3 million Kronen respectively. The imports from January to July inclusive amounted to 1779,2 and the exports to 1330,4 million Kronen, or respectively 132,6 and 7,3 million Kronen in excess of the corresponding period of 1910.

We have also to report a further increase in the sales of our goods in France, and this increase has not been restricted to those essential oils of which the preparation is one of our specialities, but has extended particularly to those costly synthetic odoriferous products, which we have placed upon the market in recent years as the outcome of our prolonged scientific investigations. At first the cognoscenti in Paris, that world-centre of the art of perfumery, were disposed to shrug their shoulders at these products of the technical development of the science of odoriferous bodies, but innumerable new popular perfumes have now proved the usefulness, nay, in many instances the indispensability of these preparations, and their future is full of promise. It is a source of great gratification to us that our synthetic floral oils in particular have gained numerous converts, especially in circles which are almost inconceivably reserved in their judgment and appreciation of the quality of such products, and that their excellence is being recognised and their advantages utilised in such quarters. We are also glad to be able to state that in the business-relations of our Western neighbours with ourselves no trace has been perceptible of that petty chauvinistic spirit which has lately pervaded a certain section of the French press; and which, but for the common sense of the reading public, might have resulted in incalculable consequences to the economic welfare of the two nations.

In the United Kingdom, trade and traffic generally have gone through difficult and vexatious times within the past six months, and even at present it does not seem as if they would be allowed to enter upon quieter waters just yet. First of all come the troubles resulting from the constitutional crisis (the question of the limitation of the Veto of the House of Lords), which caused an embittered party-struggle lasting until almost the end of August; next the prospect of internal feud consequent upon the proposed granting of Home Rule to Ireland. True, the consummation of this policy still lies in the dim future, but there is no doubt that under the stress of it political rancour will be kept at boiling-point for some months to come. Even before the coronation-festivities, which were celebrated with great pomp towards the end of June, the distant thunder of an approaching storm could be heard, and it was only the energetic and firm attitude of the great shipping-companies when confronted with a general strike which kept the harmony of those festive weeks from being disturbed by an outbreak of the revolutionary element of the populace. But when, in the month of August, the long-threatening storm actually broke and evil tidings flew across the land in quick succession, trade and industry found themselves paralysed in an incredibly short time. Railways and shipping ceased working; London, the giant-metropolis, cowered for days under the shadow of impending famine; conditions of downright anarchy prevailed in Liverpool; Manchester, Glasgow, Leeds and other towns were similarly afflicted; in short, in many places a state of things prevailed which desperately resembled Revolution. For several days the Government appeared to be absolutely powerless in the face of these disorders. Factories and shops were demolished, goods-stations stormed and set afire, police and soldiers maltreated with impunity; riotous excesses of all kinds were of daily occurrence. Everywhere chaos prevailed until at last, after long hesitancy, the unchained passions were curbed and the mob was brought to its senses by the energetic intervention of the military power. For the time being the worst seems to have been surmounted, but the inevitable after-troubles of such conditions are still felt everywhere, and unfortunately the latest news is anything rather than quieting. For the miners, numbering nearly a million, are now threatening a general strike unless their demands are conceded in full. The Board of Trade Returns for the month of August show a decline in imports of £ 1413314 and in exports of £ 2556183 as compared with the corresponding month of 1910. This decline is logically attributable to the strikes. If, in conclusion, we add to this state of things the vexatious condition of international politics, which of course reacts also upon British trade, it is really astonishing that an industrial situation involved in difficulties of such magnitude has shown no worse results so far as our branch is concerned, than has been the case in the period under review.

Business with British India has moved within normal limits, but in this market also the consumption of our manufactures is slowly on the increase. The greatest possible caution, however, is required in opening up new connections, and any manufacturer who, without regard to the reputation and commercial standing of the applicants, would respond to the requests for "free samples" which are made from every side, would certainly fail to make his trade with this country pay. The "free-sample"-hunt has almost assumed the proportions of an epidemic in India; every mail brings letters which show that the sole object of the writers is, by holding out more or less fantastic promises, to secure possession of the largest possible sample-collections. We have noticed that the same mail sometimes brings requests of this kind, couched in identical phrasing, to each one of our branch-offices. Of late business-prospects have again taken a turn for the better in India, copious rains fell in the Northern Provinces at the end of August, and, except in a few districts, have brought considerable improvement in the distressing state of affairs which had resulted from the previous failure of the monsoon. Until the end of July the rainfall in almost all parts of India had been far below the average, hence not only were the crops of most of the staple articles of export, especially cotton, placed in jeopardy, but a general rise in prices was feared. At that time the outlook was so grave that there was serious thought of abandoning the Durbar, which on this occasion is to be invested with special solemnity by the presence of the Emperor-King and his Consort. The gravity of the position was increased by the fact that the district which had suffered most severely from the drought was that of which Delhi, which is to be the principal scene of the Durbar-festivities, is the centre. The purchasing power of the people of India notoriously depends entirely upon the result of the monsoon, and so, to a large extent, does the credit of the trading classes.

Trade with Australasia has been rather dull. In this market German traders require to put forward all their energy in order to maintain and extend the connections created by untiring efforts. The bad conditions of the labour market impede the development of Australian industry and increase the cost of living of the whole population to such an extent that there is not the remotest prospect of the country competing with other nations. The Commonwealth, with a population of barely 4 500 000, suffers, in fact, from want of sufficient labour-power, and it is scarcely likely that this will be removed until the Government begins to recognise that immigration on a large scale is the only cure for the evil. Those branches of industry in which our manufactures are used also show only a very slow growth, and new undertakings with any prospect of success are very few.

There is unfortunately no ground for anticipating that the commercial crisis in Spain is about to be satisfactorily ended. After long and stormy

debates the Bill abolishing the octroi-duties has been passed by the Cortes of course under the most alluring promises that one of the first results of the measure would be a very considerable reduction in the prices of all food-stuffs, thus directly benefitting in the first place the poorer classes of the population. The loss which would accrue from the abolition of this important source of national revenue was to be made good by a proportionate increase of from 20 to 50% (!) in the tax upon house rent.

But, as is mostly the case with measures of this kind, the new Act has proved to be only a deception, for the octroi-duty has not in reality been *abolished*, but has merely been *replaced* by other and far heavier fiscal burdens. With a few exceptions, all food-stuffs have maintained their previous prices, or have even risen in price as a result of the excessive heat, and of the exceptional drought which succeeded it; therefore there can be no real question of any recuperation in the economic conditions of the country. It is feared that there will be a repetition of the farce of 30 years ago, when the octroi-duties were abolished merely to be enacted afresh afterwards, while at the same time the newly-introduced "substitution taxes" were continued. The dissatisfaction with this policy which has been growing among the people has found vent in the strikes that have broken out in almost all provinces of the Kingdom. These strikes have probably partly an economic basis, but they are also in part tinged by political agitation, and in some cases they have led to sanguinary street-fights.

The campaign which is now being carried on in Morocco finds little popular favour, and will probably cost Spain much treasure and many lives, besides causing suffering in thousands of homes for many troubled years to come.

The fact, officially admitted, that the import of manufactures into Spain during the first seven months of the current year shows a very large increase on the corresponding periods of 1909 and 1910, while at the same time the exports have fallen off very considerably, likewise bodes ill for the already unwholesome financial position of the country, and it is improbable that within the near future Spain will be able to rise out of her melancholy lethargy. Hence it is to be expected that the difficult and sluggish state of trade will continue for a long time.

In Russia, a much-coveted market for our products, the result of the harvest, according to the statistics which have just been published, is unfavourable, and in all probability the harmful effects of this misfortune will leave their imprint for some time to come upon the whole state of business in this country, which for some months past had been in every respect satisfactory.

Roumania is steadily acquiring greater importance as a buyer of our products, especially since the gratifying increase in the purchasing-power of its people which followed upon the abundant harvest of 1910, and which

of course has also brought about a considerable improvement in the conditions of credit. This season the crop-prospects are again said to be favourable, and the future of business in the country may therefore be regarded with confidence, while the best expectations of the further development of German business-intercourse with the Roumanian Kingdom seem to be warranted.

Nothing new can be reported concerning the state of business in Turkey, where, in view of the popularity in this market of "cheap" goods, the turnover has been restricted within very moderate limits. The Commercial Expert attached to the German Consulate-General at Constantinople refers to the trade in Turkey in perfumery and soaps in a report¹⁾ which will probably interest some of our friends, and of which we therefore reproduce the most important statements. The demand for perfumes, the Expert states, is large, not only on the part of foreign residents, but to an even greater extent on that of the natives of the country, for, speaking generally, Orientals are fond of perfuming themselves freely. The commoner perfumes used are mostly made by the numerous manufacturers who are established in the country itself. The import-business reached its zenith in the financial year 1906—7, but since then, owing to two poor harvests, and to the political revolution and the disturbances consequent thereon, the trade has declined to a not inconsiderable extent. It is possible, however, that it will again increase slowly but permanently. French products still maintain the first place and are sold in comparatively large quantities. An important factor in determining the sale of these goods is that novelties must be introduced every season, and here the mode of getting-up and labelling plays the most important part. Of course, the mediocre and cheap qualities have the largest sale, only the well-to-do being able to pay the high prices asked for the very best scents. As France leads in the better-class goods, so Germany holds a strong position in the sale of ordinary and medium qualities. The goods are put up according to quality in separate boxes or in boxes holding $\frac{1}{4}$ dozen or more. The ribbons, bottles and other containers should be as pretty as possible, and even for cheap scents bottles of a cut-glass appearance should be used in preference to plain bottles. The terms of payment vary; sometimes they are cash less 5% discount, sometimes against a three- or six-months' acceptance, the goods being sold inclusive of packing, f. o. b. Constantinople. Common qualities of soap are made in Turkey. What has been stated with regard to perfumes applies also to imported soaps, the sale of which has fallen off within the past few years. In this department France also probably occupies the first place, but both for quality and popularity the German soaps are fully equal to the French. The principal sources of supply are France, Germany, Austria, Britain, and the United States. Germany has not been

¹⁾ Chem. Industrie 34 (1911), No. 13.

able to get much of a footing in household-soaps, of which Britain and France supply large quantities. The selling prices of toilet-soaps run chiefly from 6 d. to 6/- per dozen cakes. There is a good market for glycerine soap, ordinary coal-tar soap and medicated tar-soap. In these varieties the German soaps are the most popular, but Italy has lately made strong efforts to gain the market, especially in tar-soaps. The better grades of soap are put up in parchment paper, tinfoil and coloured paper, the cheaper, wrapped up in paper, are packed loose in boxes and the more expensive kinds in handsome cardboard-boxes holding $\frac{1}{4}$ dozen. The usual terms of payment are cash against B/L with from 2 to 5% discount, or against 3 months' acceptance, but the term of credit is often exceeded.

The improvement in the commercial condition of Egypt has continued during the time under review, and the business in our articles of manufacture has shared therein, although the tendency to buy "cheaply" has at times made the sale of such qualities as we are in the habit of supplying very difficult indeed. The German Consulate in Cairo has published a few hints on the export of toilet-articles to Egypt¹⁾ which we reproduce textually for the benefit of those of our readers who are interested in the manufacture of perfumes. In the better classes of soap, it is stated imports from Germany show a slight decline (2074 £E in 1910, against 2556 £E in 1909), but in perfumery there has been an increase from this quarter (8341 £E in 1910 against 4687 £E in 1909). In the trade in fine soaps, Britain and Austria are ahead of Germany, and in perfumes France has a long lead. It is about 25 years ago since German manufacturers began to cater for the Egyptian market, and gradually their success became more pronounced until it reached its highest point in the years 1903 and 1904, after which, by degrees, German commerce gave way to that of other countries. In view of the fact that both the native Egyptians and the Levantines are very partial to perfumery, and considering further that some of the leading perfumery-shops in Cairo and other towns are owned by Germans, an effort should be made to gain a fresh footing in this business.

Our New York branch-house reports as follows on the state of trade in North America: —

"A characteristic feature of business in the United States in the summer of 1911 has again been the regular increase in the sales in all the multifarious branches of our business, and not only in those articles which must be regarded as special season-goods, such as for instance the materials for "soda fountain" and other "soft"-drinks, which are always largely in demand in the summer. This fact alone explains that our sales during some of the summer-months have been actually higher than those of the corresponding winter-months. Generally speaking the trend of business has been

¹⁾ Nachrichten f. Handel u. Industrie 79 (1911).

featureless. The course of prices has developed quietly and normally without any of those sudden jumps in quotations which might have served the purposes of speculators.

"The ultimate decision in the long-pending dispute concerning the customs-classification of sweet oil of orange has been in favour of the importers, but it has failed to make any impression whatsoever upon the market. The final result had been slowly discounted in the market-prices, and as at the same time prices in the producing districts began to tighten, the quotations in the United States were not only maintained, but had even to be raised shortly afterwards, because the rise in the market-value soon equalled the difference between the old specific duty of \$ 1.— per lb. and the new duty of 25% *ad valorem*.

"It may here be mentioned that a Bill for the reduction of the duties on cotton fabrics, which was laid before Congress in August last by Senator Overman of North Carolina, had been amended on its passage through the Legislature by having tacked on to it a clause amounting in effect to a radical revision of the whole Tariff-schedule for chemicals, essential oils and allied articles. Fortunately this Bill, which had been forced through both Houses of Congress just before the close of the last session, has been vetoed by President Taft. The proposed changes in the Tariff were wholly inconsistent, and had been drafted in the most superficial manner, and it is therefore to be hoped that when Congress reassembles no fresh effort will be made in this direction, as such an attempt could only have a damaging effect upon the whole development of business in our branch of industry.

"The expectations of increased business in Canada, which led to the establishment of our branch-office at Montreal, have been amply fulfilled.

"We may therefore sum up the total outlook for the winter-season 1911/12 by stating that we anticipate a further healthy development and extension of our trade, basing ourselves upon the continued application of our well-tried business-maxims, the ultimate aim of which is to gain and keep the absolute confidence of our customers."

Our New York friends have also sent us the statistical details reproduced overleaf, relating to the imports and exports of essential oils into and from the United States in the first half of the present year.

From the Argentine Republic, which is one of our most-esteemed markets, we have received regular large orders for our products, and this in spite of the unfavourable prospects to which we alluded in our last Report. We take particular pleasure in being able to trace a growing interest for goods of our standard qualities in this country. At the moment the future of business in Argentina appears in the rosiest colours, for the crop-prospects of the present year are said to be positively brilliant. As can be imagined, however, the prohibition of emigration from Italy to the Argentine has placed the last-named country in a position of the greatest

embarrassment, inasmuch as it is now confronted with the serious loss of manual labour represented by the stoppage of the yearly influx of some 60 000 Italian immigrants, and in view of the fact that the harvesting of some 22¹/₂ million acres of crops requires an army of about 135 000 labourers. Attempts are now being made to direct the flow of emigrants from other countries towards Argentina by such inducements as reductions in the fares and the opening of special credits to defray the travelling expenses of the harvesters, but at present it remains doubtful whether it will be possible to bring together the required number of suitable hands to replace the Italians.

In Uruguay the prospects just now are equally favourable. In this Republic projected new railways, especially that which is to connect Montevideo and Maldonado, will open up large tracts of fertile soil, and owing to plentiful and timely rains the harvest also promises to be parti-

Essential Oils: Imports into and Exports from the United States in the first six months of 1911 and 1910 respectively.

		Imports			Exports				
		1911	1910		1911	1910			
		\$	\$			\$	\$		
January	{	Duty-free	151 617	134 128	January	{	Peppermint Oil	26 858	13 213
		Dutiable	68 315	45 491			Other indigenous oils	34 908	14 932
							Foreign oils, duty-free	936	1 830
							" " dutiable	1 358	2 218
February	{	Duty-free	181 909	159 993	February	{	Peppermint Oil	18 396	9 602
		Dutiable	94 905	47 262			Other indigenous oils	50 532	28 284
							Foreign oils, duty-free	3 273	2 830
							" " dutiable	990	965
March	{	Duty-free	234 644	244 932	March	{	Peppermint Oil	8 666	12 030
		Dutiable	91 308	78 047			Other indigenous oils	36 973	23 425
							Foreign oils, duty-free	4 617	3 133
							" " dutiable	2 079	4 225
April	{	Duty-free	146 147	153 449	April	{	Peppermint Oil	10 435	16 644
		Dutiable	68 704	78 580			Other indigenous oils	23 249	28 651
							Foreign oils, duty-free	2 988	1 029
							" " dutiable	4 676	3 505
May	{	Duty-free	195 620	109 649	May	{	Peppermint Oil	4 044	14 393
		Dutiable	65 498	72 359			Other indigenous oils	22 127	44 159
							Foreign oils, duty-free	6 577	2 913
							" " dutiable	3 739	2 494
June	{	Duty-free	90 963	136 987	June	{	Peppermint Oil	7 218	12 461
		Dutiable	45 109	50 162			Other indigenous oils	23 459	22 187
							Foreign oils, duty-free	9 138	2 592
							" " dutiable	6 198	1 869

Total value of Imports in the 1 st half of 1911	\$ 1 434 739
" " " " " " 1 st " " 1910	" 1 310 979
Total value of Exports in the 1 st half of 1911	\$ 313 434
" " " " " " 1 st " " 1910	" 269 584.

cularly good. Assuming that there should be no plague of locusts this season, last year's loss may be expected to be made good.

There has not been much change since our last Report in the condition of trade in Cuba. It is to be hoped that the coming sugar-crop will be as abundant as were the last two, for in that case the planters, given the present high prices of beet-sugar, will do splendidly and should gather fresh courage to invest their capital in their own country.

Mexico has passed through exciting times during the last half-year. Commencing in the Northernmost districts, the Revolution gradually spread over the entire country and it soon became evident that the Government lacked the necessary strength to hold the movement permanently in check. Streams of new adherents from all quarters ranged themselves under the banner of General Madero, and before long he was at the gates of the capital. President Porfirio Diaz, recognising ere long that his position was untenable, abdicated and retired to Europe. But now all sorts of troubles have made their appearance, and for the present peace is hardly to be thought of. The Presidential elections are to be held in October and it is to be wished that the reins of government will then fall to an energetic and firm personality, and that an end will then be put to the conditions now prevailing, for in the alternative commerce will soon suffer a decided set-back, which it has so far almost escaped.

The condition of business in Brazil during the past half-year, both generally and so far as concerns the demand for the articles in which we are specially interested, may be said to have been quite satisfactory. The rate of exchange shows a further improvement, and the industries of the country, protected by a clear-sighted fiscal policy, are making gratifying progress. Increased interest has recently been shown in railway-extension schemes, as a result of which immeasurably rich regions will shortly be opened up, when it will be possible for the native industry gradually to extend its field further into the interior. It is obvious that the opening of new districts to civilisation will cause a fresh stream of immigration into the country, and the Brazilian Government is doing its utmost to attract settlers from Europe. The cultivation of corn and of rice is being steadily and successfully extended, and by degrees the Brazilians are becoming independent of the River Plate for their supplies of flour. According to the *Brazilian Review* the value of the total exports from Brazil in the first half of 1911 amounted to £ 25147565, as compared with £ 25013030 in the corresponding period of 1910. In the same period the coffee-shipments increased from £ 2895538 in 1910 to £ 11169083 in 1911, while simultaneously there was some falling-off in the values of the exports of other staple products, such as rubber, tobacco, and hides.

In Chili also the economic conditions appear to be slowly shaping towards an amelioration, and the recent noteworthy steadiness of the rate of exchange seems to indicate that the industrial and commercial recovery

of the country, which has been looked for in vain for several years, may now be regarded as within sight. It is stated in the *Deutsche Export-Review* that the Financial Commission has recently laid before the Chamber of Deputies proposals for increasing the import-duties by 10%, issuing a large loan, and gradually selling off small sections of the nitrate fields. The revenue to be derived from these sources is to be expended chiefly upon railway-construction, the remainder being used for the redemption of loans from Banks and for the re-establishment of the "financial equilibrium" of the country. Much as the last-named proposals are worthy of commendation, the suggested increase of the customs-duties would be open to grave objections if it should be intended to include our articles of manufacture, which properly ought to be classed as raw materials and which, as such, would be unable to support a further increase in price if the comparatively young national industries are to be spared what might be a serious blow.

In Peru trade and traffic continue to languish and the conditions prevailing in that country are of so unattractive a character that it is better to abstain from paying much attention to this market.

In the months immediately preceding the conclusion of the new commercial Treaty and the coming into force of the new Customs Tariff business with Japan in our articles was rather lifeless, but this is easily explained by the fact that essential oils are admitted free of duty under the new tariff, and that the Japanese importers have naturally devoted most of their attention to those articles on which the duties under the new tariff were to be raised. It is not surprising that owing to the exceptional conditions which have prevailed the value of Japanese exports as compared with the imports, has been much smaller than was formerly the case; in the first half-year of 1911 the balance in favour of imports amounted to about 104,5 million Yen.

Little that is new can be reported from China. The financial reform to which reference has been made in previous Reports, and which is so urgently needed to improve the economic condition of the country, and especially Chinese commerce, has made some further progress, the Ministry of Finance having decided, for a beginning, to strike and issue 10 000 000 standard silver dollars. The employment of our essential oils and odorous substances in China is as yet in the initial stages, because up to the present there are in that country few works which make soaps or perfumes or otherwise use articles of the kind manufactured by us. Most of these goods, especially the cheaper cosmetics, being imported ready-made from Japan, where the manufacturers are apparently better able to gauge the Chinese requirements in the matter of price and quality than European makers succeed in doing. According to *Chemische Industrie*¹⁾

¹⁾ Chem. Industrie 34 (1911), No. 12.

soap- and candle-making by machinery has, generally speaking, achieved no success, owing principally to the irrational manner in which the plants are worked and also to imperfect technical knowledge of the business. In many cases persons have been entrusted with the independent management of works whose sole qualification was that they had passed a short term of apprenticeship in Japanese works. Only two of several important plants worked by machinery have survived, namely the Hua Sheng Candle- and Soap-Works and the Tientsin Soap-Works, and these two only run full time in the spring- and summer-months. During the winter the plants lie almost wholly idle, because when the cold season sets in the demand almost comes to an end. The Hua Sheng Works were established in the year 1906 with a nominal capital of \$ 100 000. The machinery is Japanese and British, and the bulk of the raw material used is imported from Japan. The monthly output averages about 3000 boxes of soap and 1200 boxes of candles. The Tientsin Soap-Works were established in the year 1905 with a nominal capital of \$ 50 000. Their monthly output amounts to from 500 to 600 boxes of laundry-soap, 600 to 700 dozen cakes of toilet-soap and from 200 to 300 boxes of candles. Besides the above there exist a number of works which are run on a small capital and without machinery; these produce from 200 to 300 boxes of common stock soap. Among these are the firms of Kung Yih, Yiu Sheng Ho, Ho Chi, and others. So far the Chinese soap-industry has not become a serious rival to the products of the foreign, — mostly Japanese, — manufacturers, and the better-class Chinese continue to prefer the foreign goods, especially in toilet-soaps. This is confirmed by the statistics of the Chinese Customs, which show that the soap-imports last year represented a value of 200 000 Taels, equal to an increase of nearly 50% as compared with the year 1908.

Commercial Notes and Scientific Information on Essential Oils.

Almond Oil, pressed, from Almonds, G. Ph. V. The high quotations for almonds have been maintained during the summer months, an unabated and very active demand continuing for all varieties, with the result that the stocks carried over from the last crop soon approached exhaustion. We were ultimately compelled to follow suit so far as the prices of sweet almond oil of our own pressing were concerned, although we had covered our requirements at the proper time. For some considerable time the demand for this article has risen in an extraordinary degree, and to such an extent that only by continuous working of our

extensive pressing-plant has it been possible to keep pace with the orders. In all quarters our prices are willingly paid, from which we infer that those firms for whom, in the past, the article was never cheap enough, have at last acquired the conviction that almond oil is a product which should be bought from a trustworthy source, and had best be procured direct from the manufacturer. So far only superficial information of the present year's almond crop is available. In Sicily a medium result is expected, while in Apulia only a small crop is anticipated. These two districts are the main sources of supply so far as the material used by us is concerned. The prospects in Morocco are said to be favourable, but from Provence and Mallorca come complaints of the injurious effects of spring-frosts. In any case, however, the last-named district forecasts a medium crop. It is true that several weeks ago there was a very animated business in almonds for future delivery at comparatively high prices, but just lately the market has begun to sag, and we are therefore of opinion that the corresponding decline in the prices of almond oil is probable within the next few months.

Almond Oil, pressed, from Apricot kernels. Even the high quotations for Syrian apricot kernels, to which we referred in our last Report were shortly afterwards surpassed. We understand that up to within the month of July business was done at the parity of 75 *M* to 77.50 *M* per 100 kilos, and that it has been possible to maintain the high values owing to the firm tendency at Marseilles and the strong buying propensities of the Italians, although as early as the end of May it was evident that the present year's crop would be above the average. Not until the beginning of August did the price fall to about 67 *M* per 100 kilos, and so far the prices of Syrian kernels have remained at this level. If the market should not recede further, the principal reason will probably be that the Californian crop is described as a very meagre one, and furthermore that offers of Japanese and Chinese kernels have lately been almost wholly wanting. It is certain that wealthy middlemen will do their utmost to keep up the quotations. In fixing the selling-price of our guaranteed pure, cold-pressed almond oil from apricot kernels we have already taken the above-mentioned decline into account, for which reason, unless the downward movement should make further headway towards the end of the year, no further reduction is likely. Genuine *essential oil of bitter almonds* continues to be in strong demand, and the increase in our turnover, especially of the variety free from hydrocyanic acid, clearly shows that the majority of the consumers have really become convinced that our oils, although usually higher in price than competing brands, nevertheless deserve the preference. Almond oil, in fact, is an article which must largely be taken on trust, because clever adulteration is extremely difficult of detection.

G. de Plato¹⁾ has made a series of experiments with the object of investigating the conversion of hydrocyanic acid during the ripening of the almonds. His results are summarised below: In the case of bitter almonds the percentage of semi-combined hydrocyanic acid (= acid which can be eliminated by steam-distillation), gradually decreases as the fruit ripens, and disappears completely when it has attained maturity; the percentage of hydrocyanic acid in combination rises until the cotyledons are being formed, after which it decreases, (but without disappearing altogether) until the cotyledons have hardened. In the case of sweet almonds the percentage of semi-combined as well as of glucosidic hydrocyanic acid decreases when the cotyledons begin to develop, and has disappeared completely when they have hardened. As the fruit matures the nitrogen gradually assumes a stable form as albumen-nitrogen, until the fruit is quite mature, by which time 97,24% of the total nitrogen has assumed this form. This process, therefore, is the reverse of that which takes place during germination, when the albuminous bodies undergo conversion into amygdalin, the new organs requiring for their development the presence of bodies rich in energy-producing constituents. In the process of the maturing of the almonds the amygdalin may be regarded as the intermediate product in the formation of albumen. With sweet almonds the process of conversion of matter is more rapid, preventing the accumulation of amygdalin; in fact, the last-named body is used up with great rapidity.

According to P. H. Wirth²⁾, the equilibrium benzaldehyde + hydrocyanic acid $\rightleftharpoons$ benzaldehyde cyanohydrin is obtained no matter whether the reaction proceeds from benzaldehyde cyanohydrin itself or from the two component bodies. With a high degree of dilution the dissociation of benzaldehyde cyanohydrin is increased, with greater concentration it falls. When the concentration remains the same the dissociation increases as the temperature is raised, in conformity with the fact that benzaldehyde cyanohydrin is an exothermic compound. The presence of small quantities of alkalies and acids greatly affects the equilibrium-reaction, equilibrium being more rapidly attained in the presence of the OH-ion, while in the presence of the H-ion both reactions are very greatly retarded.

Under the influence of alkali the condition of equilibrium is deviated in the direction of a greater decomposition of the cyanohydrin, although fairly high concentrations are not yet followed by a complete decomposition of the cyanohydrin.

On the testing of benzaldehyde for chlorinated products, see p. 119.

¹⁾ Annali della R. Stazione chimico-agraria sperimentale 1910, Ser. II. Vol. IV. Rome 1911.
From a copy kindly sent to us by the Director, Prof. G. Ampola.

²⁾ Arch. der Pharm. 249 (1911), 382.

Oil of *Andropogon Schoenanthus* subsp. *nervatus*. In our last Report (p. 19) the parent-plant of this oil has not been stated quite correctly inasmuch as we erroneously described it as "*var. nervatus*". The correct botanical designation is *Andropogon Schoenanthus* subsp. *nervatus*, Hack.

Angelica Oils. In our last Report we had already expressed the fear that the current season's crop of angelica root would be below the mark because the young plants grown from seed sown in the previous year were not in good condition. The long-continued drought of the summer months has extinguished every spark of hope of an improved yield. The reports concerning the Thuringian plantations are really desperate, and our own angelica-fields also, which last autumn yielded such important quantities of excellent material, are this year producing next to nothing. It is therefore not surprising that the prices of angelica root oil should have suffered an appreciable increase, we are even inclined to think that the present value of about 300 *M* per kilo will not be the highest by a long way to which this important article, owing to its scarcity, will rise in the course of the next twelve months. Angelica seed oil, a product for which we have numerous buyers among our customers, is only available in small quantities the aggregate of which will certainly not be sufficient to cover the consumption until the 1912 crop is gathered in the autumn of that year.

Anise Oil, Russian. The stocks of last year's seed in the Russian producing centre had shrunk to a few wagon-loads as early as the end of May, with the result that prices advanced to about 42.50 Marks in Hamburg. This fact of itself justified the anticipation that the new crop would meet with a brisk demand at full prices, in addition to which the dry and hot weather prevailing during the months of April and May gave occasion for regarding with anxiety the further development of the anise fields. Owing to the abnormal drought the weeds, in certain districts, increased to such an extent that weeding had to be given up as useless and it became necessary to plough up the fields. To complete the misfortune, such heavy rain-showers fell at the end of July that most of the anise, just at the flowering-time, was flooded, and the setting of the fruit was completely prevented in many parts. It is obvious that in these circumstances the quality as well as the quantity of the seed must leave much to be desired. Our informants report that the crop, which finally suffered further damage in July from hot winds, will be over a month behind time the reason being that owing to the drought the young anise plants naturally made very slow growth just after the sowing. It caused no surprise therefore that when the first anise-fair was held at Krasnoie from September 1 to 11, the arrivals were exceptionally small, only 6 wagons, in fact. Although deficient in quality these supplies found buyers at very high prices. This year the area under anise amounts to about 4500 dessiatines (5270 according to another report), of which about 400 are said to have been ploughed

up, so that the actual crop-yielding area in 1911 is about 600 dessiatines less than it was in 1910. The total yield of the present season's crop is estimated at from 125 to 150 wagons, as compared with 300 wagons in 1910. These particulars should convince everybody concerned that the position of the anise market must be described as exceptionally firm, and that within the coming months higher prices may be looked forward to with certainty.

Maria Theresa Bruzzone¹⁾ has observed a case of adulteration of anise oil. While engaged in preparing *Liq. ammon. anis.* the alcoholic solution of the oil turned highly turbid with ammonia, and on being left standing the mixture gave a flocculent precipitate in large flakes. The authoress believes the anise oil to have been adulterated with a desiccating fatty oil.

Apple Oil. When a little water is poured over green apple-peel, and the material is distilled in a current of steam, according to a communication by C. Thomae²⁾, only a very small proportion of solid substance passes over; sometimes a few drops of oil are formed, the greater part of which rapidly solidifies. When the water of distillation is extracted with ether, a solid mass is obtained, which crystallises when sprinkled with alcohol. When the crystals are subjected to filtration a yellow oil with an odour of apples is obtained.

Oil of *Artemisia biennis*, Willd. From the withered and almost faded herb of this North American Composita, F. Rabak³⁾ obtained by distillation a yield of 0,03% of a deep brownish-red oil of sweetish aromatic odour and taste, which possessed the following properties: $d_{25} 0,893$, $[\alpha]_D +4,39^\circ$, $n_{D30} 1,5181$, acid v. 0, ester v. 16, ester v. after acetylation $60 = 17,28\%$ alcohol $C_{10}H_{18}O$. The oil dissolved with turbidity in 4 vols. and more of 95% alcohol. It may perhaps contain methylchavicol.

Oil of *Artemisia serrata*, Nutt. This species of *Artemisia* is also a native of North America. Rabak⁴⁾ obtained from the green, flowering plant 0,3% of a reddish-brown oil of extremely bitter taste: $d_{25} 0,913$, $[\alpha]_D +6,8^\circ$, $n_{D30} 1,4602$, acid v. 1,6, ester v. $10 = 3,5\%$ ester $C_{10}H_{17}CO_2CH_3$, ester v. after acetylation $43 = 12,2\%$ alcohol $C_{10}H_{18}O$, soluble in one-half its own vol. 80% alcohol. The oil probably contains thujone.

Oil of *Asarum europæum*. According to a note in the *Münchener med. Wochenschrift*⁵⁾ a few cases have been observed recently in which

¹⁾ Boll. Chim. Farm. 50 (1911), 468. Quoted from Zeitschr. d. allg. österr. Apoth. Ver. 49 (1911), 361.

²⁾ Journ. f. prakt. Chem. II. 84 (1911), 247.

³⁾ Midland Drugg. and pharm. Review 45 (1911), 283.

⁴⁾ Midland Drugg. and pharm. Review 45 (1911), 283.

⁵⁾ Münch. med. Wochenschr. 1910, 26. Quoted from Pharm. Zentralh. 52 (1911), 331.

the highly injurious action of oil of *Asarum europæum* (i. e. of the asarone contained therein) upon the stomach and the intestines has caused premature delivery in pregnancy.

Basil Oil, Sweet. As already stated on previous occasions, the demand for this oil for purposes of perfumery has considerably diminished of late years, and the small supplies which we have received from various producing countries have therefore been sufficient for the requirements. There has been no alteration in price.

Bay Oil. It is to be regretted that within the past six months it has not been possible to remove the difficulties in the way of procuring suitable raw material, and that we have therefore again been restricted to the use of imported oil. The few parcels of West Indian origin which have been offered were mostly of very dubious quality, and as a result some scarcity has been experienced during the past few weeks, and has already resulted in a distinct advance in prices. Higher quotations also come from the producing country, on the ground, it is alleged, that owing to some new taxation the distillation of bay oil has become much more costly. The demand for our terpeneless quality has been so lively, that owing to lack of raw material we have not always been able to meet it.

Betel Oil. H. Gilbert¹⁾ describes the cultivation of the betel-plant in the Province of Thanh-Hoa (Tonquin). According to this author there are two varieties of the plant, of which one attains a height of from 6 to 9 feet and the other of up to 30 feet. The last-named is the cultivated variety.

The betel-plant grows best on rich soil, such as the loamy borders of rivers. As the condition of the leaves is the principal consideration when the crop is gathered and as the leaves are very sensitive to the influence of the weather, it is necessary to protect the plants against wind and sun, for which reason they are grown under large shelters, built of bamboo sticks and covered with bamboo-matting. These shelters being rather expensive to construct and to keep in repair, the cultivation of the betel-plant is somewhat restricted. The plant is propagated from cuttings which are planted out in holes from 4 to 6 inches deep, and staked to the bamboo-sticks which form the support of the shelter. Planting takes place in March, April, or May, and the crop may be gathered the same season. Oil-cake, especially cotton seed cake, is used for manuring.

Birch Bud Oil. The few small parcels of birch buds which have been offered from Russia during the present year have been kept at such high prices that we have been compelled to make a corresponding increase in our quotations. Unfortunately, from the point of view of quantity also the supplies are unequal to the demand, and the consumption has there-

¹⁾ Journ. d'Agriculture tropicale 11 (1911), 227.

fore been restricted primarily to oil of the previous season. At the present time the stock has already been reduced so seriously that it is hardly likely to suffice until the spring of next year.

Buchu Leaf Oil. Since April last there has been no change whatever in this article, which only plays a secondary part at the present day, inasmuch as the scarcity of buchu leaves still persists. It is said that buyers in the United States are prepared to pay prices for buchu leaves which for us are altogether outside the range of practicability.

From the leaves of *Barosma crenulata*, L. we obtained 1,7% oil possessing the following properties: d_{150} 0,9364, α_D -- $15^\circ 22'$, n_{D20} 1,48005, soluble in 2,5 vols. and more 70% alcohol, with elimination of paraffin. The original oil was coloured green by copper, but after removal of the metal it was brownish yellow. The odour was mint-like (menthone?), the diosphenol content was exceedingly slight, and when the sample was placed in a freezing-mixture only paraffin separated out.

In an English contemporary¹⁾ a new species of buchu-leaves is mentioned, which is probably derived from *Barosma venusta*. This species differs from *Barosma pulchella* in its leaves, which are rounder in shape and have no odour of citronella. When the leaves are crushed between the fingers a pungent, acrid odour appears, which, after some time, recalls that of anise and fenugreek.

Oil of Buphane disticha. According to F. Tutin²⁾, the alcoholic extract of the bulb of *Buphane disticha*, Herb. (N. O. Amaryllidaceæ), a native of South Africa, yields a small percentage of an essential oil which contains furfural.

Oil of Bupleurum fruticosum. The oil of *Bupleurum fruticosum*, L., an umbelliferous plant which grows wild abundantly in the island of Sardinia, has been described by L. Francesconi and G. Sanna³⁾. The material was distilled in various stages of maturity and in different localities. The constants of the oil were as follow: d_{150} 0,8257 to 0,8692, $\alpha + 19,72$ to $45,50^\circ$, n 1,4783 to 1,4862, sap. v. 5 to 14, sap. v. after acetyl. 23,7 to 28,5. The oil-yield varied from 0,5 to 4,4%.

The oil consisted chiefly of hydrocarbons; it contained only small proportions of alcohols and esters. It was found that the oil-content increases as the plant reaches maturity, and that the flowers contain more oil than the leaves. Plants gathered at high altitudes contain more oil than do those from the plains. The density, optical rotation and index of refraction increase as the plant develops; they attain their maxima

¹⁾ Chemist and Druggist 78 (1911), 854.

²⁾ Proceed. chem. Soc. 27 (1911), 149.

³⁾ Gazz. chim. ital. 41 (1911), I. 395. Quoted from Journ. Soc. chem. Ind. 30 (1911), 921.

during the flowering-period, at the end of which they diminish again. The ester-content of the leaves diminishes during the flowering and is largest in the plants from the mountains. The leaf-oils contain more ester than do the flower-oils; plants grown in a moist atmosphere are deficient in ester. The sp. gr. of oils rich in ester is higher, and their rotatory power lower than that of oils which are deficient in ester. The flowers contain a larger proportion of free alcohol than the leaves and during the flowering period the content of free alcohols increases at the expense of that of the alcohols in combination.

Cajuput Oil. We may complete our previous report by stating that the exports of cajuput oil from Macassar in the year 1910 reached 1739 baskets, compared with 1488 baskets in 1909, and that about one-half of the shipments went to the United States. So far as any figures are available for the present year, the shipments appear to have slightly declined, and if in spite of that the prices have receded somewhat, this only affords a fresh proof that the article is suffering from restricted demand. The cheap eucalyptus oils, and especially our pure eucalyptol, which we are able to offer on such favourable terms, now constitute competitors of cajuput oil, the importance of which should not be underrated.

Oil of Calamintha Nepeta. Two oils¹⁾, distilled in Dalmatia from *Calamintha Nepeta*, Savi (*C. Nepeta*, Clairv.; *C. nepetoides*, Jord.), gave constants similar to those of a distillate from the same plant described by us on a previous occasion²⁾, The oils were of a yellowish colour, possessed a mint-like aroma, and, for the rest, behaved as follows:

I. d_{15}^0 0,9305, $\alpha_D + 2^\circ 50'$, n_{D20}^0 1,48441, acid v. 0,9, ester v. 5,4.

II. d_{15}^0 0,9395, $\alpha_D + 6^\circ 28'$, n_{D20}^0 1,48920, acid v. 0,9, ester v. 14,6.

From 2 to $2\frac{1}{2}$ vols. 70% alcohol were required to effect a solution. The pulegone-content of sample No. 1 was determined with neutral sodium sulphite and found to be about 45%.

Camphor Oil. Very little that is new has happened in the camphor oil market during the last few months. As before, the United States have continued to be the principal buyers, and have occasionally been willing to pay prices for which there was really no justification in view of the marked quietness of the camphor market and the falling tendency of turpentine oil. For the moment scarcely any camphor oil is offering, but in spite of this fact prices have not become materially firmer. Both in Europe and in the U. S. large supplies of crude oil are available, and the existence of these affords some security that for some time to come no surprises are to be feared. Moreover, as stated above, there has been a not inconsiderable reduction in the prices of turpentine oil. Hence it is hardly

¹⁾ See p. 63, footnote 2.

²⁾ Report October 1906, 14.

likely that from this quarter there will be any inducement for an advance of camphor oil, which most frequently serves as a substitute for turpentine oil. In spite of this reduction, however, the demand for the various grades of light and heavy camphor oil has continued to be extremely brisk at unchanged prices, which clearly proves that these oils have everywhere become indispensable; that, as compared with the numerous other turpentine oil substitutes, their employment offers certain advantages; and finally that in certain cases camphor oil is to be preferred even to turpentine oil.

According to a report from the British Consul at Tamsui¹⁾ which has just been published, the energetic action by the Japanese Government against the savages in the interior of Formosa has had the result of opening up in the north of the island an extensive forest district, rich in camphor trees. Several important native tribes were overthrown at the end of 1910 or have voluntarily surrendered, so that in the course of the present year a new and important region has been made available for Japanese civilization. The quality of the camphor trees is said to vary considerably in the different districts. The camphor oils which are prepared from the trees in the north are decidedly richer in camphor than those prepared from the trees in the south, — hence the opening-up of the northern forests is of special importance. The Japanese Government continues to support the planting of new camphor trees by placing trees from the Government schools of Forestry at the disposal of the planters. The distillation of camphor oil from the leaves is still in the experimental stage. As in previous years, the entire production of camphor oil in Formosa was sent to Japan in 1910 to be worked up for camphor.

According to the same source, the exports of camphor from Formosa in the year 1910 were as follows: —

United States	2 942 800 lbs.
Germany	1 808 000 „
France	908 667 „
United Kingdom	542 400 „
India	249 333 „
Japan	35 072 „
Total: 6 486 272 lbs. (Value £ 404 112.)	

It is further reported that last year the Japanese camphor refiners had to pay 5 yen 80 sen (= 11/10½ d.) per 100 kin (133 lbs.) more for their crude camphor than was paid by their competitors in Europe and America, and that in consequence they started an energetic movement for the purpose of inducing their Government to sell crude camphor within the Japanese Empire at the same price as abroad. It was pointed out that the cost-price of camphor was of great importance in view of the fact

¹⁾ Diplomatic and Consular Reports, August 1911, No. 4769.

that the manufacture of celluloid has recently been started in Japan, and that camphor is the principal raw material for this manufacture. In the meantime the Government of Formosa has ordered the price of camphor for shipment to Europe to be raised, as from 1st April 1911, from £ 5. 5/- to £ 7. 10/- per case.

A chapter in the *Yearbook of the U. S. Department of Agriculture*, by S. C. Hood and R. H. True, contains particulars of the present position of camphor-cultivation in the United States, of which an American periodical¹⁾ publishes an extract, dealing principally with the yields which have been obtained thus far and with the prospects of the future development of the plantations. It is stated that an examination of 1000 trees in the States of Florida, Alabama, Louisiana, Texas, and California revealed considerable variations in the yield of camphor from leaves and from branches. For instance, a few trees which had grown up in the shade of other trees or of high buildings only yielded 0,70% of crude distillate, whereas other trees, which had grown on poor soil and had received no care, yielded up to 2,77% distillate. These figures, however, represent the extremes on either side; as a general rule a yield of from 1,75 to 2,25% may be expected, calculated on green material. The crude oil contains from 75 to 80% pure camphor, which thus equals an output of from 1,35 to 1,50%, calculated on green material. This yield may be increased by trimming the trees, and especially by growing them in hedges. To such an extent is it possible to increase this yield, that the output obtained up to the present from hedge rows grown at distances of 15 feet (space between the separate trees 6 feet; height of the trees 8 feet), amounted for each of the two trimmings which were made yearly to 8000 lbs. of green material per acre, corresponding to a total yield of pure camphor of from 175 to 200 lbs. yearly. The planting of camphor trees is specially recommended on light, sandy soil, such as is found in many parts of the Southern States, especially in Florida. At the same time it is desirable, in view of the high cost of transport, to erect a distillery, and if possible also a refinery, in immediate vicinity to the plantation. In order to keep such a plant going rationally a plantation of at least 200 acres is required. The cost of production calculated per pound is of course less when operations are conducted on a large scale, and it may be assumed that a plantation of 500 acres would be sufficient to warrant the production of camphor at the lowest possible price.

In our Reports of October 1906, p. 20, and April 1907, p. 22, we mentioned the results of an examination of a sample of camphor oil from German East Africa, which had been forwarded to us by the Imperial

¹⁾ Oil, Paint and Drug Reporter 79 (1911), No. 22, p. 41.

German Biological-Agricultural Experimental Station at Amani. At the beginning of last year we received for examination another sample of this oil, which resembled the first. We subsequently communicated the results of our investigation to the above-mentioned Institute by letter. Lommel¹⁾ has now published the details of our analysis, together with those received from other investigators.

D. E. Hutchins²⁾, lately Conservator of Forests, communicates some interesting information on the natural occurrence of camphor-trees in German East Africa. According to this authority, the camphor-tree is abundant and shows a good natural production in a forest situated in the neighbourhood of Wilhelmstal and leased by a Mr. Wiese. At one place in the West Usambara Mountains, for example, Hutchins counted 26 seedlings of camphor on 20 square yards. Their appearance, he states, was more vigorous than that of the suckers which constitute 99% of the reproduction in British East Africa. Unfortunately, Hutchins omits to state whether the tree is botanically allied to the true camphor-tree (*Cinnamomum Camphora*). Hutchins regards it as curious that neither the botanical staff at the Imperial German Biological-Agricultural Institute at Amani nor the forest officials at Wilhelmstal had recognised the tree.

Hutchins' article deals mainly with the timber-resources of the forest, to exploit which Mr. Wiese employs about 1000 natives. In the wetter parts of the forest four-fifths of the timber consists of the valuable outeniqua yellow-wood ("East African Kauri"). The cedar-tree, of which there is an apparently inexhaustible supply, forms the principal source of revenue in these forests.

The Journal from which we take the above particulars points out that, some years ago, Hutchins, on behalf of the British Colonial Office, investigated the potentialities of the forests of Kenia, British East Africa, and on that occasion reported on the occurrence there of the "Ibean camphor-tree"³⁾ but that nothing appears to have been done since then to confirm the camphor-bearing properties of that tree.

As a result of the fall in price of natural camphor which took place some time ago, the manufacture of the synthetic article of course received a heavy blow. An editorial article in a French journal states⁴⁾ that a (French?) company which controls several processes relating to the manufacture of camphor has circularised its shareholders to the effect that the cost of production of synthetic camphor must be kept as low

¹⁾ Der Pflanze, Zeitschrift für Land- u. Forstwirtschaft in Deutsch-Ostafrika 7 (1911), 133.

²⁾ Agricult. Journ. Brit. East Africa. Quoted from Chemist and Druggist 79 (1911), 18.

³⁾ Comp. Report October 1907, 26.

⁴⁾ Journ. d'Agriculture tropicale 11 (1911), 156.

as possible, and that with the prices now ruling for the raw material, turpentine oil, it is impossible to make the manufacture pay. The company, however, was in possession of a new process for the preparation of a cheap turpentine oil, for the carrying-out of which it was intended to float a subsidiary company. The writer of the editorial comment asks how it would be possible by such means to bring about a considerable reduction in the cost-price of synthetic camphor without causing first of all a general reduction in the price of turpentine oil as a result of the working of the new process, and he enquires whether, for this reason, it would not be more remunerative to sell the new cheap turpentine oil as such, instead of using it to prepare artificial camphor.

Camphorwood Oil, spurious. In a previous Report¹⁾ we referred to the fact that we had been able, from so-called "spurious camphorwood oil" to isolate an aldehyde showing a remarkable similarity to the aldehyde prepared by us from the oil of *Perilla nankinensis*, the only difference being that the rotation was reversed. Since then, Semmler and Zaar²⁾ have more closely examined the oil (which we had placed at their disposal), with the result that they have found the aldehyde of the "spurious camphorwood oil" to be identical with d-perillic aldehyde. This fact was proved by conversion into d-limonene as well as by the preparation of the oxime and of perillic acid³⁾. d-Perillic aldehyde was isolated with sodium bisulphite and found to possess the following constants: b. p. 99 to 104° (9 mm.), d_{180} 0,965, $[\alpha]_D + 135,6^\circ$, n_D 1,50803. In addition to d-perillic aldehyde the oil contained myrtenal⁴⁾, an aldehyde which had been prepared some years ago by Semmler and Bartelt by oxidising myrtenol, but which was not hitherto known to occur in any essential oil. In order to isolate the myrtenal the oil was shaken up with neutral sodium sulphite. From the sulphite solution, which had previously been rendered alkaline, the aldehyde was driven off by steam, when the perillic aldehyde remained in solution — probably as a non-volatile hydrosulphonic acid derivative. The purified myrtenal possessed the following properties: b. p. 89 to 92° (11 mm.), d_{200} 0,9859, $\alpha_D + 13,6^\circ$, n_D 1,50618. The semicarbazone had m. p. 230°. From the myrtenal oxime (b. p. 125 to 128° at 9 mm.; d_{210} 1,0292; $[\alpha]_D + 42^\circ$; n_D 1,53803) the authors prepared the myrtenal nitrile which, when saponified, yielded myrtenic acid: m. p. 54°, b. p. 149 to 152° (9 mm.), d_{220} 1,0712, n_D 1,50618.

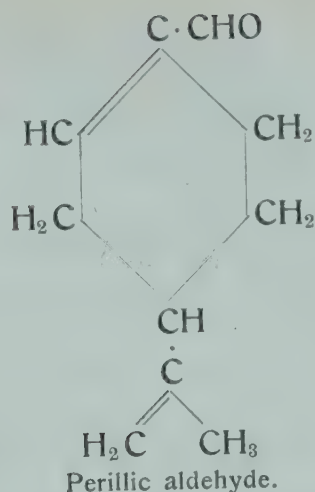
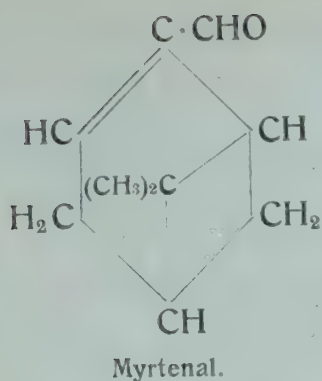
The joint occurrence of perillic aldehyde and myrtenal in "spurious camphorwood oil" is most interesting, because the mutual relations of these two aldehydes are the same as those of pinene and limonene.

¹⁾ Report October 1910, 146.

²⁾ Berl. Berichte 44 (1911), 815.

³⁾ Comp. Report April 1911, 76, 93.

⁴⁾ Berl. Berichte 40 (1907), 1363; Report October 1907, 64.



In addition to cineol, of which the presence was ascertained by us, the oil contains d-limonene, identified by preparing the tetrabromide (m. p. 103 to 104°).

Cananga Oil. Various reports of impending scarcity which obtained currency in the course of the summer having proved unfounded, the position of the article may be described as unchanged, and as we have been able to enlarge our already considerable stock by advantageous purchases, we believe ourselves to be justified in stating that the present range of prices will probably remain stable within the near future.

Caraway Oil. It may be said for certain that caraway is the only important raw material of our industry which has not suffered from the abnormal conditions of the weather this year, — at any rate so far as the quantitative yield of the crop is concerned. As early as the middle of June, the Dutch Ministry of Agriculture reported that everywhere the caraway crop was looking healthy and thick, in the province of Noord Holland it was even described as being "very good". A further report published by the same Department on July 15 gives the area under caraway this year as 8236 hectares, compared with 7692 in 1910 and 7114 in 1909. Up till that date the plants had developed well and in many parts threshing was about to begin. The yield as well as the appearance of the caraway was thoroughly satisfactory, and the crop was described as "good", in Groningen as "good to very good". According to information gathered by our correspondents the yield per hectare is said to have been from 40 to 50 bales, and the total yield at least 20000 bales. The preliminary conditions for a reduction in price were therefore in existence, and the market did, in fact, recede to about 11 Fl. per 50 kilos. Soon, however, a brisk turnover for future delivery caused the position to become firmer, especially in view of the expectation that the caraway plantations will be greatly restricted next year. The farmers assert that when caraway does not fetch more than 11 Fl., other produce pays them better, and they therefore intend again to take up other crops. The result of the caraway

crop would have warranted a decided lowering of the prices of oil, but for the fact that the oil-yield of the seed turned out to be far below the average. We have therefore been able to make only a moderate reduction in our quotations, and in the face of the market position depicted above we regard a further fall as out of the question. Moreover, in the last few weeks the market has acquired increased firmness, because the caraway sown this year, which will produce the 1912 crop, has been severely injured by the continued heat. We would again call attention to the fact that our various caraway oils, by reason of our perfected distilling-process, possess the finest aroma imaginable, and that no such disappointments need be feared with them as frequently attend the employment of so-called "cheap" caraway oil.

We print below the comparative statistics of the past two seasons, as published by the Dutch Ministry of Agriculture, and in continuation of the table which appeared in our last October Report.

Province	Cultivated area hectares		Yield per hect. in bales of 50 kilos		Total yield in bales of 50 kilos	
	1910	1909	1910	1909	1910	1909
Groningen	2,696	2,024	22,9	25,8	61,723	52,259
Friesland	68	50	25,4	24,2	1,726	1,212
Utrecht	5	10	22,0	20,0	110	200
Noord-Holland	2,517	2,806	22,2	23,4	55,872	65,785
Zuid-Holland	252	276	23,4	22,6	5,906	6,232
Zeeland	1,291	1,131	26,8	24,1	34,653	27,275
Noord-Brabant	863	817	23,0	23,0	19,822	18,777
Entire country	7,692	7,114	23,3	24,1	179,812	171,740

Caraway-growing in Holland is the subject of an article by van der Wielen in the *Pharmaceutisch Weekblad*, No. 35, 1911¹⁾. Besides numerous historical details, the article contains statistical data, as well as a description of caraway oil and of the method of adulterating it.

Cassia Oil. This important article has remained in a condition of comparative listlessness throughout the summer, and only insignificant price-fluctuations, from 3/3 up to 3/5 per lb., were to be recorded. As is always the case, 80 to 85% oil was most in demand, but the trade has not exceeded the limits of a healthy requirement for actual consumption and the market has not been influenced by any speculative undertakings. Whereas formerly cassia oil of all manner of degrees of quality was offered and dealt in, the offers have lately been restricted to 75/80 and 80/85%.

¹⁾ From a reprint kindly sent to us.

oil, which shows that the method of valuation which has been advocated by us for over 20 years has really brought about an improvement in the conditions of quality, and that by degree users have acquired the conviction that the price of inferior qualities has always been too high as compared with that of the better grades.

The U. S. Consul at Swatow¹⁾ has recently sent in a report on a new cassia-growing enterprise in China. He states that last year Huang Hsi-ch'uan, who is a Hakka and a member of the Chinese provincial assembly, has instituted a series of experiments in cassia-culture at Kaying, in the course of which it was found that the soil and climate there were very suitable for the growth of this plant. Huang Hsi-ch'uan had previously carefully studied the corresponding conditions at Wuchow, on the West River, where there are large cassia-forests, and accordingly he formed a company known as the "First Kaying Company for the cultivation of Cinnamon" and started a model plantation, not only, it is said, with a view of making money from the undertaking, but especially in order to promote industrial enterprise and to counteract the tide of emigration among the people of the region. Two species of cassia are grown in the new plantations, one large and the other small. The former flowers when 10 years old, but it is only cut down at the age of 20 years for the purpose of harvesting the bark. Between the ages of 10 and 20 years only the seed, of which the value is small, is harvested. The smaller variety yields leaves for the manufacture of oil at 3 to 4 years of age, and its bark is only harvested at the age of 6 or 7 years. As soon as the trees (and this applies to both varieties) are cut down, new shoots immediately spring up around the stumps, so that such a plantation, once started, lasts practically indefinitely. The wood is used for fuel, the wood-ashes and the small twigs are employed for medicinal purposes, the bark yields the "cinnamon" of commerce, and from the leaves oil is distilled. According to the Chinese text, "a yellowish earth, light and dry", is the most suitable soil; it requires no fertilisers. The trees are not much affected by drought. The seed is sown in a kind of nursery, and the young trees are transplanted when two years old. A picul of seed ($133\frac{1}{3}$ lbs.) costs \$ 120 to \$ 130 Mexican (\$ 50.76 to \$ 55 American currency) and contains about 20 000 000 seeds, while 10 000 saplings cost \$ 40 Mexican (about \$ 16.92 American currency). The Consul's report goes on to state that the Chinese text, so far as it relates to the prospective returns, is not quite clear, but it appears to make the following estimate: "10 000 trees will yield annually as a by-product some 7 piculs (933 lbs.) of leaves, worth 60 cents Mexican (\$ 0.25) per picul. This would seem to refer to dead leaves, which can be plucked from time to time without retarding the growth of the trees, for it is stated that 10 000 leaves (presumably young

¹⁾ Daily Consular and Trade Reports, July 3rd, 1911.

green leaves), harvested when the trees have been cut, will yield 40 catties (53 $\frac{1}{3}$ lbs.) of oil. The value of the oil is estimated at \$ 1.40 to \$ 3.— Mexican (\$ 0.59 to \$ 1.27 American currency), per catty. Ten thousand trees will yield 2000 catties (2667 lbs.) of bark worth \$ 160 to \$ 260 Mexican (\$ 67,68 to \$ 109,98) per 1000 catties. Ten thousand catties (13 333 lbs.) of wood, after being burnt, will yield 50 catties (66 $\frac{2}{3}$ lbs.) of "soda", which is used as medicine. A site near the Han River has been selected as a nursery, and under the supervision of a specialist seeds and saplings have been procured from Foochow and Lo-ting-chow. The company estimates that by 1918 it will have a plantation of 800 000 trees, and that only seven labourers will be required to tend a plantation of 100 000 trees, their wages amounting to from \$ 50 to \$ 60 Mexican (\$ 21,15 to \$ 25,38) per man per year. According to a recent newspaper report the sub-prefect of Kaying, accompanied by the shareholders, paid a visit of inspection to the plantation, much to the satisfaction of the neighbours, and found that of the seeds already bought about 70 p. c. had sprouted.

We have thought it right to bring this (in parts very obscure) report to the notice of our readers, in particular because information from the cassia-growing districts with regard to the conditions of production is so very scarce. The estimate of the wages strikes us as being of special interest, for according to it a Chinese labourer would earn from 85/- to 105/- of our money yearly. For the rest we must, of course, await the further development of the undertaking before it will be possible to judge whether it will in any way affect the cassia oil market.

Celery Oil. We hear that the French celery seed crop has turned out a very scanty one, and that prices are being realised which are quite out of proportion to the previous value of the article. We have consequently already been compelled to advance our quotations for the oil, and as it seems certain that great scarcity will make itself felt within the next few months, we regard a further material rise in the market as more than probable.

Chamomile Oil, German. Although the chamomile crop, especially in Hungary, has this year been very plentiful, and there was every reason for expecting very low prices for the distilling material, values nevertheless maintained their position owing to the brisk demand, and in the circumstances there is no question of any reduction in the quotation of our pure distillate. Moreover, the time of collection, especially in Germany, was very restricted owing to the abnormal drought, and at its conclusion a corresponding improvement in the market became perceptible, more particularly in the growing districts in Hungary.

Chamomile Oil, Roman. Owing to the exceptional heat and drought which have visited England this summer in common with other countries, it was impossible for the English chamomile cultures to develop in a

satisfactory manner, with the result that we are now faced with a complete failure of the crop. It follows as a matter of course that the prices of Roman chamomile oil have had to be increased, and as things are it appears to be certain that the production of this year, together with the small remaining supplies of last season, will not be sufficient to last until the next crop. It is therefore probable that there will shortly be fresh increases in the price. Experiments made by us at Miltitz in the cultivation of Roman chamomile have also been much affected by heat and drought, but generally speaking all the preliminary conditions for the successful growing of the plant appear to be fulfilled, and we intend next year to continue our planting and distilling experiments.

Chlorocodon Root Oil. Some years ago Goulding and Pelly¹⁾ described a body melting between 41 and 42° which they had obtained by steam-distillation from chlorocodon root (probably *C. Whiteii*, N. O. Asclepiadaceæ), a plant which is a native of Uganda. P. Friedländer²⁾ afterwards identified this compound as p-methoxy salicylic aldehyde.

We recently received from Africa a root which, when distilled with steam, yielded 0,34% of a body which consisted mainly of the solid substance described above, in addition to small quantities of a brown oil. It dissolved readily in ether and alcohol, and sparingly in water. Recrystallised from the latter (or better still from dilute alcohol), it afforded white, lustrous needles, m. p. 40 to 42°. The aqueous solution assumed a reddish-brown colour with ferric chloride. The entire distillate had a very obtrusive odour, perhaps somewhat resembling that of rhubarb, while the crystals, when purified by repeated recrystallisation, reminded of coumarin. These data warranted the surmise that the drug examined by us was also a chlorocodon root. Anatomical comparison with the root investigated by Goulding and Pelly (a sample of which had been courteously supplied to us by the Imperial Institute in London), confirmed this surmise, but it was not possible to decide positively whether both roots belonged to the same species. Only two species of *Chlorocodon*, however, are known, viz., *C. Whiteii*, Hook. f. and *C. ecoriata*, N. E. Br. The former occurs in Natal and elsewhere in South Africa, the latter in the region of the Congo and in tropical East Africa.

Cinnamon Oil, Ceylon (G. Ph. V). Within the past few months cinnamon chips have continued to show only slight fluctuations, and quite recently it was even possible to buy at somewhat reduced rates. The prices of our pure distillate have remained unaltered, and as we are well-supplied with raw material for a long time ahead, we do not, at the moment, apprehend an advance in the quotations within the near future. We distil cinnamon oil on the largest possible scale and are therefore

¹⁾ Proceed. chem. Soc. 24 (1908), 62; Report November 1908, 196.

²⁾ Monatsh. f. Chem. 30 (1909), 879; Report April 1910, 173.

in a position to supply the article as advantageously as possible. For large contracts we are in a position to make some slight reduction on our list-prices.

Citronella Oil. The quotations of Ceylon citronella oil (Schimmel's test) had for a long time been in the neighbourhood of 10 d. cif., but within the last few months a firmer tendency has gradually become perceptible, and under its influence the quotations finally advanced to 1/- up to 1/2 d. cif. European ports. This tightening of the prices is somewhat difficult to understand, especially in view of the fact that as a rule July and August are the very months in which the largest arrivals come forward in Ceylon, and also because in our opinion the demand both in Europe and in America has not improved, but on the contrary, has if anything fallen off. It is possible that the parties interested believe themselves justified in raising their quotations on account of the not inconsiderable decrease in the exports during the first 7 months of the present year, for the latest available figures relating to the citronella exports from Ceylon are as follows:—

From 1 st January to 21 st August 1911	915 683 lbs.
In the corresponding period of 1910	1 070 732 „
„ „ „ „ „ 1909	1 106 731 „

The above figures show that the deficiency of the present year's exports compared with those of 1910, to which attention was already drawn in our April Report, has not, as might have been expected, been equalized. The sluggish state of trade which has prevailed in this article in recent months should have been sufficient to show that there could be no question of any increase in the demand, and the raising of the prices could therefore at best be due to artificial manœuvring, unless indeed the higher requirements as to quality which have been set up within the past few months have caused the native dealers to raise their ideas of the value. However this may be, we are inclined to think that the present firm tendency will not be of long duration, and that if prices should nevertheless rise still higher, the large soap-makers, who are the principal consumers, will find it easy to turn to other articles which after all are not more expensive than citronella oil.

The pure Estate oil with a geraniol-content of 57 to 62%, which was introduced by us in the spring of the present year, has already secured a number of regular buyers, but generally speaking this exquisite quality is not by far esteemed as it deserves to be. To our regret we have even observed that, curiously enough, the very firms of soap-makers, especially in England, who formerly were always the first to insist upon certain standards of quality, and who were in the habit of referring to the insufficiency of "Schimmel's test", are now, when we have succeeded in procuring at a low rate an oil which answers their requirements, taking little or no notice of this new quality.

Java citronella oil has continued to be available in such ample quantities that we have even been enabled somewhat to reduce our prices. We beg to seize this occasion to call attention to the exquisite quality of our brand, which for delicacy of aroma and richness of yield is unsurpassed. We are regularly in receipt of important consignments, and for the present are still in a position to make special quotations for large quantities.

A method for the acetylation of citronella which originally appeared in the *Chemist and Druggist*¹⁾, and which has recently been reprinted in an American contemporary²⁾, has inspired a searching criticism by C. Kleber³⁾. First of all Kleber corrects the assertion which is made in the description of this method that the acetate of sodium is added for the purpose of absorbing the water formed in the course of esterification with acetic anhydride. As a matter of fact, the sodium acetate merely plays the part of a catalyser, for since no water whatever is formed in the course of the reaction, none can be absorbed. Moreover, every trace of water which might be present would be absorbed, not by the sodium acetate, but by the acetic anhydride, with generation of a corresponding quantity of acetic acid; hence, in order to obviate errors, Kleber expressly recommends the use of *fused* instead of dry sodium acetate, on the ground that the ordinary crystalline salt, although it looks dry, in fact contains 3 molecules of water of crystallisation, which would effect the decomposition of a portion of the acetic anhydride.

Further, according to Kleber it is impracticable to wash out the acetylated product with water, because too many washings would be required to remove the acid completely. The object is much more quickly attained, he states, by shaking once with a solution of common salt, running off the aqueous solution, and completing the neutralising process with a 10% carbonate of soda solution, which should be added in small portions, the mixture being vigorously shaken each time. The completion of the reaction is indicated by the cessation of pressure in the separating funnel after shaking⁴⁾.

When the oil has been acetylated and washed out it must not be dried with anhydrous sodium bisulphate, as laid down in the *Chemist and Druggist*, but with anhydrous sodium sulphate, because the first-named agent, owing to its acid properties, might split up the geranyl esters. Warming on the water-bath also is not only superfluous but positively objectionable. Half an hour is not enough to saponify the ester which is formed; the oil should be left upon the water-bath at least one hour, two hours is still better.

¹⁾ *Chemist and Druggist* 77 (1910), 896. Also comp. Report April 1911, 46.

²⁾ *Americ. Perfumer* 6 (1911), 86.

³⁾ *Ibidem* 116.

⁴⁾ Comp. Gildemeister and Hoffmann, *Die ätherischen Öle*, 2nd Ed. Vol. I. p. 595.

Kleber next refers briefly to the geraniol-test, the general introduction of which for commercial purposes would scarcely, in his opinion, afford the universal panacea against adulterations which it is claimed to be by others. Kleber specially holds this view because the practised sophisticator would find ways and means of imparting to his oil the required acetylation-value by means of esters, alcohols (fusel oil, &c.) and acids, and because the "average pharmacist", judging blindly by the acetylation value, would fail to detect such additions.

Another English periodical¹⁾ now enters the field with proposals relating to the testo which Ceylon citronella oil should be required to meet. It demands that the constants of the oil shall be as follows: —

d_{150} 0,898 to 0,910,

α_D — 7 to — 13°,

acid content (calc. as acetic acid) not to exceed 0,25%,

acetylisable constituents (calc. as geraniol) not less than 58%,

soluble in 2 to 3 vols. 80% alcohol; the solution must remain

clear up to an addition of 10 vols.

With regard to these suggestions we wish to point out that the maximum limit of the sp. gr. should be raised to 0,915 at least; we have occasionally — although very exceptionally — known it to be still higher (up to 0,920). The maximum limit for the rotation has also been fixed too low, for only recently we examined samples of guaranteed pure oils expressly distilled for us in Ceylon, which gave only — 16°. It would likewise be impossible to maintain strictly the requirements relating to solubility, rather would it be necessary to admit that the diluted solution may turn slightly opalescent, for an absolutely clear solution is an exception.

In connection with the fixing of constants, the journal referred to also gives a prescription for the determination of geraniol, which, although differing somewhat from that in its precursor, the *Chemist and Druggist*²⁾ shows an equal determination to pass by in silence everything that has recently been published on the subject of the acetylation of citronella oil³⁾ and to set up some "special method". There can be no doubt that our own prescription, *which is founded upon an experimental basis*, must be familiar to the English chemists who are concerned in this matter, and it is therefore surprising that in spite of this knowledge they should again persist in taking a course of their own. Such a proceeding certainly cannot help the problem forward. We can only repeat again and again that in the case of citronella oil in particular it is necessary to work by a clearly defined method if it is desired to obtain results which shall correspond

¹⁾ *Perfum. and Essent. Oil Record* 2 (1911), 172. Also comp. *Chemist and Druggist* 79 (1911), 387, and *Pharmaceutical Journ.* 87 (1911), 361.

²⁾ *Chemist and Druggist* 77 (1910), 896.

³⁾ Report April 1909, 36; April 1910, 156.

the actual percentage of total geraniol in the sample, and which shall be comparable with each other. In our last Report¹⁾ we gave a detailed account for our method, the trustworthiness of which has been proved by tests with mixtures of known geraniol- and citronellal-content, and we may therefore content ourselves here with a reference to that Report. It goes without saying that in our laboratories our estimations are exclusively made according to this method, for which reason we refrain from quoting the English method here.

Clove Oil. From the latest report of the British Consul in Zanzibar²⁾ we reproduce a few tables which may be welcome to our readers in completion of the statements made in our last Reports. With regard to table A, it should be added that the remarkable decline in the clove exports to England is due to the fact that of late large parcels have been sent to the U. S. direct without transshipment in British ports, and also that considerable quantities of cloves declared as destined for Hamburg and Rotterdam, ultimately find their way to British ports as a result of "optional transshipment".

The probable result of the present year's summer crop was at first the subject of the most contradictory rumours, but this is the case every year, and it is only within the last few weeks that the position has been cleared up to this extent, that it has become quite certain, from announcements made in the Zanzibar Government Gazette of 18th July, that a plentiful yield may be expected.

According to a report of the German Consul-General in Zanzibar, which has only lately been published in the Official German reports of Trade and Industry³⁾, the result of the clove crop in the last harvest-year (August 1910 to June 1911) has been a quite exceptionally poor one. According to statistics now published it amounted to 191 303 frazileh (1 frazilah = 35 lbs. English). This crop has been the worst but one since 1895/6, having been only surpassed in smallness by that of the year 1903/4. The prospects for the crop of the coming harvest year (August 1911 to June 1912) on the other hand are very favourable, according to a statement published by the Government of Zanzibar in its Official Gazette of 18th July, and it is to be expected, says this authority, that the yield of the abundant crop of the harvest year 1908/9, amounting to 615 418 frazileh, will be exceeded. It is probable that the crop will be gathered early, and that therefore considerable quantities of cloves will already be brought to market within the near future. The gathering will probably be in full swing in the month of October.

¹⁾ Report April 1911, 46.

²⁾ Diplomatic and Consular Reports 1911, No. 4716.

³⁾ Nachrichten f. Handel u. Industrie 1911, No. 96.

A. Exports in the years 1908—1910.

To	1908 Cwts.	1909 Cwts.	1910 Cwts.	1908 £	1909 £	1910 £
United Kingdom . . .	20 389	16 004	5 052	40 005	27 030	14 335
British India . . .	61 312	62 329	59 106	121 944	113 314	139 946
Netherlands . . .	5 003	26 826	15 053	9 447	47 475	28 828
United States . . .	5 841	21 115	9 787	12 305	39 330	20 240
Germany . . .	29 438	40 162	19 440	59 119	74 079	37 354
France . . .	8 205	9 302	1 683	15 050	16 725	3 950
Austria-Hungary . .	759	2 054	629	1 456	3 557	1 415
Italy . . .	538	2 049	1 005	926	3 591	2 337
Other countries . .	2 219	1 275	2 380	4 708	5 309	5 065
Total	133 704	181 116	114 135	264 960	330 410	253 470

B. Deliveries of the last 15 years.

Year	Zanzibar Frazileh	Pemba Frazileh	Total Frazileh
1896	119 787	237 090	356 877
1897	90 676	240 954	331 630
1898	60 363	308 485	368 848
1899	139 320	344 764	484 084
1900	49 180	248 935	298 115
1901	49 977	294 709	344 686
1902	58 438	235 106	293 544
1903	146 308	172 811	319 119
1904	36 550	387 846	424 396
1905	91 448	374 893	466 341
1906	189 198	209 211	398 409
1907	179 137	460 051	639 188
1908	141 850	299 952	441 802
1909	102 225	435 000	537 225
1910	93 814	221 420	315 234

C. Deliveries in the last 14 harvest years.

Harvest year	Zanzibar Frazileh	Pemba Frazileh	Total Frazileh
1896—97	84 592	224 362	308 954
1897—98	44 941	150 703	195 644
1898—99	149 417	481 565	630 982
1899—1900	59 741	206 640	266 381
1900—01	37 567	201 192	238 759
1901—02	43 626	321 599	365 225
1902—03	175 420	251 780	427 200
1903—04	28 369	96 792	125 161
1904—05	79 860	675 683	755 543
1905—06	181 539	109 931	291 467
1906—07	56 833	202 633	259 466
1907—08	213 667	541 998	755 665
1908—09	165 733	449 685	615 418
1909—10	109 682	300 043	409 725

If this official prognostication should prove well-founded, the yield of the year 1911/12 would rank third or fourth in point of abundance since the year 1895/96, being only surpassed by the yields of the years 1907/8, 1904/5 and possibly 1898/9.

Laudis and Hartz¹⁾ report on the treatment of consumptives with clove oil. The hypodermic administration of the oil being painful, it was given internally according to the following prescription:

Oleum Caryophyllorum, Syrupus Senegæ aa 7,1;
Extractum Glycyrrhizæ 42,6; Aqua destillata q. s. ad 75.

M. Sig. Three times daily one teaspoonful after meals.

In numerous cases good results were obtained, the troublesome cough being reduced, and occasionally an improvement in the general condition of the patient was manifested. Clove oil also increases the appetite.

Coriander Oil. On the whole the prices of this oil have remained unchanged during the past summer, and it is only lately that a pronounced stringency in the market has become perceptible. Only about 100 dessiatines are under coriander in Russia, and, as in the case of anise, so the abnormal climatic conditions are said to have very adversely affected the development of the plants. It is said that the crop has been practically a failure, only from 70 000 to 80 000 kilos having been gathered, and as there are no other countries which produce coriander fit for distilling, we advise our friends to exercise the greatest economy with their stocks of coriander oil during the coming season. As a matter of course, the prices have already been considerably increased.

Costus Root Oil. Contrary to expectation the working-up of the parcels which reached us in the spring has yielded a highly favourable result, and we are therefore able, in spite of the high price which we have paid for the root, to offer our guaranteed pure distillate at very favourable rates. There is no doubt that prices will be maintained for some considerable time to come, for higher rates have lately again been asked for raw material from India. We have covered our requirements for a long time ahead, and herewith beg to call special attention to our favourable quotations.

Cubeb Oil. It has only been possible to make a slight reduction in price since our last Report, and that merely because we have succeeded in securing a large parcel of cubebs on advantageous terms, which gave a highly satisfactory yield. The cubeb market continues to be controlled by the United States, and the prospects continue to be firm, as all parcels which are being offered for sale realize full prices.

¹⁾ Zentralbl. f. d. gesamte Therap. 1910, No. 8. Quoted from Pharm. Zentralh. 52 (1911), 355.

Curcuma Oil. E. Rupe¹⁾, who has occupied himself for some considerable time with researches on the constitution of curcumone and of its oxidation-product, curcumatic acid, and who has drawn up a series of formulæ for the latter, has prepared synthetically, in collaboration with J. Bürgin²⁾, *p*-tolylmethylethyl acetic acid, which may possibly be identical with curcumatic acid. Although the acid possesses the same b. p. as curcumatic acid it differs from the last-named in the result of oxidation with permanganate of potassium, for whereas in this reaction curcumatic acid yields *p*-tolylmethylketone and a dicarboxylic acid (m. p. 227°), *p*-tolylmethylethyl acetic acid gives rise to another ketone, perhaps tolylethylketone, and to a mixture of two acids, probably *p*-acetylbenzoic acid and terephthalic acid.

Cypress Oil. Although we have taken the precaution of working up large quantities of green cypress leaves in our factory at Barrême, in order to make sure of being able to cope with the increasing demand for this excellent and well-tried remedy against whooping cough, we would suggest to our customers that they should lay in their requirements betimes, because in case a whooping cough epidemic should occur during the late autumn, the oil might easily become scarce, the more so because our New York branch, after efforts extending over many years, has at last succeeded in interesting numerous American medical men in the remedy, and a brisk demand for the United States is therefore to be anticipated.

Essential Oils, Sicilian and Calabrian.

With his usual obligingness, our esteemed friend Mr. Eduardo Jacob of Messina has sent us the following report, dated September 6th: —

In my Spring-report I had already pointed out the strong probability that in the course of the season all our Sicilian and Calabrian essential oils would attain high prices, but nobody could have the remotest conception of the height which the quotations would actually reach.

The causes which existed for what may be described as an abnormal advance in prices in all essential oils have their roots in the first place in the unfavourable conditions of production which prevailed during the past winter, and next (and this was also an important factor) in the circumstance that during the last three years our manufacturers have made a good deal of money, and thus have acquired greater powers of resistance and a higher degree of independence from the commercial demand.

It is due to the last-named fact that notwithstanding the extremely sluggish course of trade which resulted from the high prices of all oils these oils not merely maintained their values, but have shown a steadily increasing tendency from the commencement to the present time.

¹⁾ Comp. Report April 1908, 36; October 1909, 53; April 1911, 56.

²⁾ Berl. Berichte 44 (1911), 1218.

Turning to the different varieties of essential oils, I have to report as follows:—

Bergamot Oil. In the previous Report attention has already been called to the fact that the last bergamot-crop was a very moderate one indeed.

As no old stocks worth mentioning had been carried over into the new year from the last few crops, the steady and continuous demand from abroad resulted in a strong upward movement in the price of bergamot oil, and in spite of the fact that the demand has fallen off in the course of the last four months this tendency has been maintained.

At the end of March the prices of bergamot oil stood at 32 to 35 *с/л* per kilo according to the ester-content of the parcel, but during the summer they leapt up by several stages to from 43 to 46 *с/л*, in spite of the fact that a certain proportion of the would-be users, owing to the elevated prices, had cast about and actually found substitutes for the article.

Several reasons can be adduced in explanation of the fact that bergamot oil now stands at a level which it had not attained for more than half a century previously. First of all, the quantity of this oil produced here during the last three years has been less than in the three years preceding the earthquake. Secondly, it may be boldly assumed that formerly adulteration of the oil was much more common than is the case nowadays. The falling off from this cause in the quantity of oil which would formerly have been considered fit for export may be estimated as fully 15 to 20%. Another decline of 10% is due to the fact that after the earthquake of 1908 a number of bergamot-gardens were uprooted to provide for the erection of new wooden settlements and villages in the immediate proximity of the old heaps of ruins. It may therefore be safely assumed that, supposing the conditions of the crop to be equal, from one-fourth to one-third less bergamot oil is now available for purposes of trade than was the case say four or five years ago. To this must be added that the owners of bergamot-plantations and the manufacturers of the oil have made a good deal of money in recent years owing to the steadily advancing prices and are now, taken as a body, very prosperous and even wealthy, so that they are better able to keep back their produce and turn it to good account than they used to be.

About three months still separate us from the new crop, and the quantity of oil available for prompt delivery is so exceedingly small, nay, insignificant, that until the arrival of the new crop no important reductions in price are to be expected. From the beginning the prospects of this crop have warranted no rosy illusions. In a few small parts of the growing-district it is hoped that the yield will equal about 60% of that of last season, but the greater part of the gardens only promises half a crop and in certain localities the machines will not be required at all this year, as the trees are bearing no fruit, having been severely damaged during the winter by frost and loss of foliage.

So far there has been no talk of any business in new bergamot oil for delivery in January 1912; on the one hand sellers are wanting because the garden-owners ask enormous prices for the fruit, and on the other buyers are likewise absent, nobody being willing to transact business at the high rates. If the oil-content of the fruit should be high, it is not impossible that next year's prices will fall below the average of those of the present season; but if the fruit should be poor in oil, the output of bergamot oil will be very small indeed, and it will hardly be possible for the price of the article to recede, inasmuch as some of the users of bergamot oil are unable to employ substitutes and even the limited consumption from this source would suffice, given such a small crop, to keep prices here at a high level.

Lemon Oil. When we wrote in the middle of March last, we left lemon oil at the price of 9 *ℳ* per kilo cif. Trieste; at the present moment we find it quoted at from 14.50 *ℳ* to 15 *ℳ*, an advance equal to about 65% on the value.

Special stress should be laid upon the fact that on the present occasion the buyers abroad have only had to bear the smallest part of this advance. The burden of the difference in price has fallen chiefly upon the shoulders of the exporters here, who at the commencement of the season, without being covered themselves, had foolishly entered upon contracts for delivery with foreign buyers at low prices, and who have had to pay the penalty of their imprudence as the season progressed. Buyers abroad, amply covered for five or six months ahead by their cheap purchases, were for a long time indifferent spectators of the rising market, while gradually consuming their own low-priced supplies. But now that these stocks have come to an end, the foreign consumers are compelled, as their needs dictate, to concede the high rates now ruling. The pronounced speculative tendency of our market throughout the entire season has imparted greater firmness to the article, and made it possible for the market to maintain itself in spite of the counter-operations which have been set on foot by a few export-firms who had entered into engagements for the shipment abroad of very large quantities at low prices. Our local speculators and most of the large manufacturers, who have made large profits in the article during the last few years, are ably and effectively supporting the market by buying up and storing for speculative purposes during the manufacturing season all the excess of supplies which is being offered for sale. The result of these operations is to obviate accumulation upon the daily market of an excess of supplies which might depress the prices of the oil. Just at present the holders of oil have the game in their hands.

The remaining available stocks of old oil are very small, and can hardly be estimated at more than 30000 kilos, all of which will doubtless find its way abroad within the next 3½ months.

When the time of production of the new oil arrives, therefore, no old oil-supplies of any importance will be in existence here, and as once more the new crop only promises to yield an ordinary average result, it is most probable that even if the prices of the new oil in the course of the coming season do not remain at the present abnormally elevated level, they will at any rate keep very high when compared with the average quotations of the past three years.

The quotations for new oil for delivery, shipment January/March 1912, opened at 8 *ℳ* per kilo, but quickly advanced to 9 *ℳ*, and have since then been forced up to 11 *ℳ*. At the time of writing there are no sellers at that figure, but plenty of speculative buyers.

As already stated above, the new crop promises to be about equal to last year's. The greater or less oil-content of the fruit and the question whether the demand from abroad for boxed lemons will again be as animated as it was last year, are factors which will need to be taken into consideration so far as the oil-output of the present year is concerned, and which may determine whether a larger or a smaller quantity of oil will be manufactured.

Mandarin Oil. In the spring this oil attained its highest price of 105 *ℳ* per kilo, since when it has ultimately receded, so far as the still existing trifling stocks are concerned, to 95 *ℳ*. The new crop again leaves much to be desired, but in any case it is better than last year's. At the present moment the manufacturers ask 50 *ℳ* cif. Trieste for new oil for delivery in December and January.

Orange Oil, Bitter, has kept at a level of from 15.50 *ℳ* to 16 *ℳ* throughout the whole of the past season. Hardly any stocks of old oil remain in existence. The new crop, like that of sweet oranges, promises to be small.

Orange Oil, Sweet. The small crop of last year has been the cause of the rise, amounting to about 40%, which has taken place in this oil in the course of the summer. No speculative incursions affecting the natural course of the article have to be recorded; rather has the price advanced slowly from 12 *ℳ* towards the end of March to its present level of 18 *ℳ* per kilo, the rise keeping pace with the gradual diminution of the available supplies in sympathy with the call from abroad.

While the world's consumption of lemon and bergamot oils shows an increase, it would appear that the demand for sweet orange oil has diminished in recent years, in spite of the fact that, generally speaking, the prices of the article have been low, only the present year, on account of the smallness of the crop, having been an exception in favour of the oil.

The stock of old orange oil is probably entirely cleared at the present time, except for a few small lots in the hands of owners whom no price will satisfy.

Unfortunately it has to be reported that the new orange-crop looks very poor indeed. The trees have suffered from frost last winter, and the flowering has on the whole been scanty, and in its turn, has produced but little fruit. It is therefore expected that the new season, which begins early in October, will witness high prices.

Sales for October/November delivery have been made on the basis of 17 *M* cif. Trieste, but at the present time no one is any longer willing to sell at this figure. It is difficult to say whether, next season, the oil will find ready takers abroad at such high prices, or whether the consumption will show a further restriction and leave the manufacturers with their stocks on hand until, by concessions, they make the buyers more willing.

Bergamot Oil. An interesting contribution to the subject of the adulteration of essential oils is supplied by Parry¹⁾ in an account of the recent examination by himself of an "artificial bergamot oil". Taken by itself, such an examination would be without interest, for there are many artificial bergamot oils on the market nowadays, but the oil referred to by Parry attracts attention from another point of view, because the manufacturers, a well-known Paris firm, offer the article for sale without any concealment, both at Paris and in the bergamot districts of Southern Italy as an avowed adulterant of bergamot oil. A covering circular letter accompanying the invoice, which, together with a sample of the oil, reached Parry from a business friend, and which is published in Parry's article, is reproduced below because it is desirable that the spirit of unscrupulousness which finds expression in this document should be put into the pillory as often as possible. The circular, translated literally from the French, reads as follows: —

"Sir, — I acknowledge the receipt of the order you gave to my traveller when visiting your town, for which I thank you, and for which you will find invoice enclosed. At the same time I send you a duplicate invoice containing the details of the labels and declaration for customs purposes. I beg you to conform to these indications, for, in this manner, the product being declared as "chemicals" you will only have a small duty to pay. I am convinced that you will be well satisfied with this product, which possesses a specific gravity 0,885; rotatory power about $+18^{\circ}$ to $+20^{\circ}$; ester v. about 38 per cent.; solubility in alcohol, normal; residue on evaporation 6 to 7 per cent., which is equivalent to saying that, from the analytical point of view, no observation can be made as to the presence of this product. So far as concerns the perfume, it is very sweet, and very easily covered by the pure

¹⁾ *Perfum. and Essent. Oil Record* 2 (1911), 59.

essence of the peel. The name "terpinyl acetate", chosen from the declarations, is to be understood as merely a matter of convenience, for the product is a totally different thing from terpinyl acetate. Awaiting your news, and always at your command, receiving, sir, my sincere salutations,

A—— B——."

Further comment is unnecessary. According to Parry's description the oil in question was a green-brown, sweet-smelling substance, but its odour was not exactly that of bergamot oil. Among its constants the rotatory power in particular differed altogether from that mentioned in the manufacturers' circular. Parry found the following values: d_{15}^{20} 0,8885, n_D^{20} 1,36°, apparent ester v. 40%, fixed residue 6,2%.

From his further examination Parry concludes that the preparation is probably concocted from limonene, linalool, terpinyl acetate and an ester of the type of ethyl citrate, and he regards it as the most dangerous adulterant of bergamot oil which he has met so far, because when it is mixed with an equal volume of bergamot oil a very excellent imitation of the pure oil results.

We may add to the above that if the composition of the article really agrees with Parry's description of it, it should not be such a very difficult matter to detect this "artistic" artificial compound.

Lemon Oil. We have been struck by the fact that several firms have lately again been offering lemon oil with a guaranteed citral-content of from 6 to 7 p. c. Years ago several English chemists¹⁾ as well as ourselves²⁾ called attention to the worthlessness of such a guarantee, and we can only repeat to-day that according to the experience which has been gained in the meantime it is impossible to guarantee a definite citral-content for lemon oil, because on the one hand this factor is subject to certain fluctuations, and, on the other, the result depends altogether upon the method of estimation. In confirmation of these statements we set forth below the citral-content of lemon oil as ascertained by the different chemists who have investigated the article. Soldaini and Berté³⁾: 6,5 cc. in 100 cc. oil; Parry⁴⁾: 5 to 6%; Burgess and Child⁵⁾: 4 to 7%; Gulli and Stavenhagen⁶⁾: 7 to 7,3%, rarely less than 6,5%; Parry⁷⁾: 3%; Sadtler⁸⁾: 5,26%; Kremers and Brandel⁹⁾: 4,2%; Berté¹⁰⁾: 6,85 to 7,4%.

¹⁾ Chemist and Druggist **63** (1903), 277, 341.

²⁾ Report October **1903**, 34.

³⁾ Boll. Chim. Farm. **35** (1899), 527; Report April **1900**, 25.

⁴⁾ Chemist and Druggist **56** (1900), 376; Report April **1900**, 24.

⁵⁾ Journ. Soc. chem. Industry **20** (1901), 1176; Report April **1902**, 23.

⁶⁾ Chemist and Druggist **63** (1903), 401; Report October **1903**, 34.

⁷⁾ Chemist and Druggist **63** (1903), 820; Report April **1904**, 47.

⁸⁾ Americ. Journ. Pharm. **76** (1904), 84; Report April **1904**, 48.

⁹⁾ Pharm. Review **22** (1904), 15, 72; Report April **1904**, 47.

¹⁰⁾ Chem. Ztg. **29** (1905), 805; Chemist and Druggist **66** (1905), 682; Report October **1905**, 28.

Romeo¹⁾: 3,64 to 4,48%; Rother²⁾: 5,25 to 5,9%; Bruylants³⁾: 2,86 to 6,47%; A. H. Bennett⁴⁾: 4,3 to 5,2%; Chace⁵⁾: 4,1 to 7,0%.

Some years ago we ourselves, working by a method communicated to us by a friend of our firm, but which has not been published, have found warranted pure lemon oils to contain from 4,3 to 7,2% citral⁶⁾, but in the course of time we have become convinced that the results obtained by this method, in its original form, may in part have been too high, for after further improving the method we only obtained values fluctuating from about 4 to 5%.

What has been said above should suffice to show that in view of the far too insufficient degree of reliability of the majority of the various methods of estimation, the guaranteeing of a definite citral-content in lemon oil is a matter of quite subordinate importance, especially because that content is subject to natural variations. Furthermore, it is probable that in pure oils the citral-content does not reach 6 to 7%, as is conspicuously stated to be the case by certain firms. In the face of such recommendations the conviction involuntarily imposes itself that they are only made to mislead buyers. We regard it as wrong to attach special value to a definite and if possible very high citral-content in lemon oil, for inasmuch as this factor varies in pure oils, and only amounts to a few per cent., slight adulterations do not show themselves in the citral-content, while serious adulterations are much more readily detected by the ordinary methods of examination.

Mandarin Oil from unripe fruits. A sample of oil has been sent to us from the Province of Valencia in Spain, which was pressed from green unripe mandarins (mandarinettes), and in view of the fact that oil from this material was unknown up to the present it may here be briefly described. The oil was of a deep olive-green colour and possessed a pleasant aroma, less delicate, however, than that of oil pressed from ripe mandarins. Its constants also deviated somewhat from those of the latter: d_{15}^0 0,8665, n_{D20}^0 1,47900, acid v. 0,2, ester v. 17,3, evaporation-residue 8%. Owing to the dark colour it was impossible to read the rotation of the original oil; the angle of rotation of the initial 10% of the distillate was $\alpha_D + 55^\circ 12'$. The oil was not completely soluble in 90% alcohol, but it made a clear solution with one half its own vol. a. m. 95% alcohol.

¹⁾ *Un nuovo metodo di determinazione quantitativa del citral*. Messina 1905. Report October 1905, 30.

²⁾ *Die Bestimmung der Aldehyde und Ketone zur Bewertung ätherischer Öle*. Inaug. Dissert., Dresden 1907; Report October 1907, 120.

³⁾ Bull. de l'Acad. roy. de Belgique (Classe des sciences), Nr. 3, 1907, 217. Annal. de Pharm. 13 (1907), 321; Report October 1907, 122; April 1908, 168.

⁴⁾ Analyst 34 (1909), 14; Report April 1909, 110; October 1909, 153.

⁵⁾ Journ. Americ. chem. Soc. 28 (1906), 1472; Report April 1907, 116; April 1910, 64.

⁶⁾ Report November 1908, 60.

According to our observations the characteristics of mandarin oil pressed from the ripe fruit are as follows: d_{150} 0,854 to 0,859, $\alpha_D + 65$ to 75° , α_D of the initial 10% of the distillate a little lower, or up to about 2° higher, than α_D of the original sample; n_{D200} 1,475 to 1,478, acid v. up to 1,7, ester v. 5 to 10, evaporation-residue 2,4 to 3,5%.

Orange Oil, Sweet. In an article entitled "le droit de conclure", G. Courtz¹⁾ attacks the judgment given by a German laboratory on a sample of sweet orange oil. The sample in question was found to be abnormal in a peculiar manner so far as its more than usually dark colour and its high evaporation-residue were concerned, but it was held that deliberate adulteration could only be surmised when such adulteration could yield a pecuniary advantage and that this was not the case with the sample under investigation, first of all because it came from a different district than the ordinary oil of commerce, and secondly because the addition of only about 3% of foreign matter could not be held to be due to financial considerations.

The German Laboratory referred to by Courtz being our own, we will briefly explain matters here. One of our clients submitted to us for our opinion a sample of sweet orange oil weighing only a few grams. Our analysis showed the following characteristics: d_{150} 0,8535, $\alpha_D - 91^\circ 38'$, α_D of the initial 10% $+ 93^\circ 0'$, evaporation-residue 8,8%. We therefore gave it as our opinion that the specific gravity and the optical behaviour of the oil agreed with those of bitter orange oil, and that, moreover, the abnormally high evaporation residue and the characteristics of that residue made it probable that the oil had been adulterated with a fatty oil. The firm which had supplied the oil protested against this finding, and as a result we asked for, and received, a larger parcel of the oil in order that we might make a more thoroughgoing investigation. The oil now gave the following constants: d_{150} 0,8555, $\alpha_{D200} + 92^\circ 24'$, α_D of the initial 10% $+ 98^\circ 4'$, evaporation-residue 9,5%.

The difference in the constants of the two samples was to be explained by the fact that when the bottle containing the first sample was rinsed out with spirit, a little alcohol had got into the oil, but could no longer be detected. As regards the constants of the second sample, only the rotation of the initial 10% corresponded to that of the values which had been found by us for pure sweet orange oils²⁾, while the other constants were incompatible with purity. Subsequent exhaustive examination of the evaporation-residue showed without a doubt the presence of a fatty substance.

In contradistinction to the evaporation-residue of pure oils of orange, the residue of the sample under examination made a clear solution with

¹⁾ Parfum. moderne 4 (1911), 68.

²⁾ Report April 1911, 72.

light petroleum, while it was insoluble in its own vol. of warm alcohol. Its acid value was lower and its saponification value higher than that of pure oil, and it contained only about 3% of non-saponifiable matter as compared with about 20% in pure oil, while its glycerol content was six times that of pure oil. The saponaceous matter yielded by it made a clear solution with water after evaporation of the alcohol: with pure oil the solution was turbid. The fatty acids contained a smaller proportion of volatile and a larger proportion of solid constituents than is the case with pure oil. They were crystalline, pale brown and opaque, as compared with the dark-brown, wax-like and transparent fatty acids of pure oil.

For purposes of comparison we admixed 7% cotton oil to a sample of sweet orange oil, and we record below the comparative analytical values of the two samples: —

	Sweet orange oil	After addition of 7% cotton oil	Sample of oil under exam.
d_{150}	0,8498	0,8549	0,8555
α_{D20}	+ 97° 2'	+ 90° 46'	+ 92° 24'
α_D of the initial 10% . .	+ 96° 50'	+ 96° 14'	+ 98° 4'
Evap.-residue	2,7%	9,8%	9,5%
Sap. v. of evap.-residue	149,4	182,9	171,4

The colour of the sample under examination was in our opinion rather paler than that of pure sweet orange oil, and as the evaporation-residue of pure oil is at most 4%, and it followed that about 5½% of fatty substance had been added, we were forced to pronounce the oil as sophisticated, particularly so because, when allowance is made in the constants of the oil for the percentage of fatty matter referred to above, the constants of the sample would agree in every respect with those of sweet orange oil.

By analysis we identified as such the fat contained in the oil without a shadow of doubt, and no one can doubt that the addition of 5½% of an adulterant means a pecuniary benefit. For the rest it is quite immaterial for purposes of a verdict whether the addition is intentional or accidental: in any case the fact remains that the oil under examination contained several per cent. of fatty matter which has nothing to do with it.

Estragon Oil. Owing to the drought, our own fields have only yielded small quantities, which are hardly likely to be sufficient to cover the requirements until next summer. Consumers will have to prepare themselves for higher prices.

Eucalyptus Oil. There has been no change whatever in the position of the eucalyptus oil market within recent months; the demand for all varieties having continued fairly brisk at unchanged low rates. For several years past, Australia has been the sole source of supply of the oil, and in view of the depression in prices there seems to be no probability of distilling being resumed in other parts.

In the *British Medical Journal* W. E. Foggie¹⁾ refers to a case of poisoning by eucalyptus oil. A six-year old boy, two hours after being given a teaspoonful of eucalyptus oil, was seized with colic, vomiting, and diarrhoea. Three hours later the patient began to lose consciousness, followed by collapse, but after 2 to 3 hours more the boy recovered completely. No attack upon the kidneys was observed.

As already mentioned in our last Report²⁾, eucalyptus oil has lately been used extensively in Australia in the smelting of ore. A business-friend of ours there has recently supplied us with a few further particulars on this subject, which we reproduce here as a matter of general interest.

Last year enormous quantities of oil have been consumed in the mining-districts in the processes of preparing sulphides of zinc and lead. About $\frac{1}{2}$ lb. oil is emulsified by vigorously shaking it up with about 100 gallons water, and with this mixture the moistened or powdered ore is stirred up. The eucalyptus oil absorbs the sulphide-particles and carries them to the surface, together with the gold and silver contained in them, up to 95% of the actual content of the powdered ore being recovered by the process. The Barrier Mines already consume about 10 tons of eucalyptus oil monthly, and this exceptional demand makes the distillers independent of other markets.

Oil of *Fagara xanthoxyloides*. As mentioned by us in our last Report³⁾, Thoms, some time ago, reported upon the pharmaco-chemical examination of the root-bark and fruit of *Fagara xanthoxyloides*, Lam. [*Zanthoxylum* (*Xanthoxylum*) *senegalense*, D. C.; N. O. Rutaceæ]. Since that time detailed particulars have been published concerning the examination, which was carried out by H. Priess⁴⁾. From this publication we abstract the following details: The peel contains about 2.4% essential oil of a brownish colour and a faintly acid reaction (d_{15}^0 0.9229; $[\alpha]_{D_{15}^0}$ — 1.20°; acid v. 2.19; ester v. 58.51) from which, with sodium bisulphite, methyl-n-nonylketone was isolated. For the purpose of identifying the ketone the author prepared the oxime (m. p. 45 to 46°) and the semicarbazone (m. p. 120 to 121°). It is probable that the ketone is mixed with an alde-

¹⁾ Brit. med. Journ. 1911, 359. Quoted from Therap. Monatsh. 25 (1911), 339.

²⁾ Report April 1911, 72.

³⁾ Report April 1911, 73.

⁴⁾ Berichte d. deutsch. pharm. Ges. 24 (1911), 227.

hyde, perhaps decylic aldehyde. Oxidation of the ketone-fraction resulted in *n*-caprinic acid.

Treatment of the oil with potash liquor led to the isolation of the lactone xanthotoxin, a body melting between 143 and 144°. This compound may be obtained in considerable proportions by extracting the peel with alcohol. The nitro compound of xanthotoxin ($C_{12}H_7O_4NO_2$) melts at 230°, the dibromo compound, recrystallised from xylene, at 164°. When an alcoholic solution of xanthotoxin is diluted with potash liquor a salt, soluble in water, is formed, a yellow colour ensuing.

Of acids, the oil contained *n*-caprinic acid, both in the free state and in combination (m. p. of the amide 98°). The saponification liquor furthermore contained acetic acid, as well as a solid acid which was not examined more closely.

Other constituents of which the presence was proved were dipentene (m. p. of the tetrabromide 124 to 125°), linalool (m. p. of the citryl- β -naphthocinchoninic acid 198 at 199°), and a sesquiterpene with the following properties: b. p. 170 to 180° (14 mm.), d_{140} 0,9214, $[\alpha]_D + 4^\circ 16'$. No hydrochloride of this sesquiterpene was obtained.

In the pharmacognostical part of his investigation Priess reviews the examinations of the various *Fagara*-species which have so far been carried out, and in the course of this he also refers to the oil from "Wartara seeds" described by us. As we were uncertain at the time whether our material was of a uniform character, we caused the fruit to be examined by Dr. Giessler. That authority informed us that the "Wartara seeds" distilled by us were derived from *Xanthoxylum acanthopodium*, D. C. No fruit of other *Fagara*- or *Xanthoxylum*-species was admixed to the sample.

Oils of the following *Fagara*- and *Xanthoxylum*-species have now been described¹⁾:

- Fagara aubertia*, D. C. (*Evodia aubertia*; *Xanthoxylum aubertia*)²⁾,
- Fagara Naranjillo*, Engl. (*Xanthoxylum Naranjillo*, Grisebach)³⁾,
- Fagara nitida*, Roch. (*F. piperita*, Lown; *Xanthoxylum nitidum*, D. C.),
- Fagara octandra* (Blanco)⁴⁾,
- Fagara Peckoltiana*, Engler⁵⁾,
- Xanthoxylum acanthopodium*, D. C.⁶⁾,
- Xanthoxylum alatum*, Roxb.⁷⁾,

¹⁾ Linnæus' two genera, *Fagara* and *Xanthoxylum*, which had been amalgamated for a considerable time, have recently been separated once more by Engler (Engler-Prantl, *Die natürlichen Pflanzenfamilien*, Vol. III, Sect. 4, p. 115).

²⁾ Report April 1907, 105.

³⁾ This plant contains a terpene (Flückiger, *Pharmacognosie*, p. 661).

⁴⁾ Report April 1905, 82.

⁵⁾ Berichte d. deutsch. pharm. Ges. 9 (1899), 340.

⁶⁾ Report April 1900, 50; April 1901, 59.

⁷⁾ Report October 1910, 147.

Xanthoxylum fraxineum, Willd. (*X. ramiflorum*, Michx.; *X. tricarpum*, Hook.; *X. clava Herculis*, Lam.; *X. caribæum*, Gaertn.; *X. americanum*, Mill., and

Xanthoxylum piperitum, D. C. (*Fagara piperita*, L.; *Piper japonicum*)¹).

Fennel Oil. By tactful manœuvring the Galician speculators have thus far succeeded in keeping the prices of fennel seed at a level which was really out of consonance with the favourable result of last year's crop. The policy adopted has been always to place only just enough seed on the market to satisfy the demand, and thus to obviate a depression of prices as a result of too plentiful a supply. At first the prospects of the present year's crop, — which is about a month late, — were very favourable, but recently there have been complaints that unusually heavy rains have greatly damaged the plants and that only a good medium crop can be looked for. It is therefore to be expected that during the winter some, if only a slight, weakening of prices will take place, especially as the quantity of seed carried over into the present season is said to be by no means unimportant. The German fennel crop in our neighbourhood (Lützen) has been a complete failure, but its output does not affect our branch of industry.

Geranium Oil. The accuracy of our view concerning the course of prices of African geranium oil continues to be justified by events. The scanty offers with which the Algerian producers are making their appearance in the open market are so extraordinarily high that users cannot be blamed for gradually and increasingly eliminating African geranium oil from their recipes and replacing it by suitable substitutes, such as pure geraniol and others. The last quotations were at the rate of from 40 frcs. to 42 frcs. per kilo, but only small parcels were being offered. As already previously stated, the low prices of two or three years ago have induced several of the largest growers to give up their geranium-cultures and to replace them by more profitable crops. In view of the fact that, all alarmist rumours and manipulations notwithstanding, the prices of Réunion geranium oil cannot be driven up beyond the limit of about 36 frcs., the position is not of a character to give fresh courage to the Algerian distillers, and it need therefore occasion no surprise if the shipments of African oil in the present year should fall considerably below even those of the year 1910. Up to the end of July they have totalled to 18 200 kilos, whereas for the entire year 1910 they amounted to 33 700 kilos.

The position of Réunion geranium oil has gradually undergone considerable change in the course of the summer, reports of discontinuance of plantations, destruction of the crop by hurricanes, and so forth, having succeeded each other. As a result the quotations have risen considerably. The latest market-report which has reached us from St. Denis is dated

¹) Report October 1890, 61.

from the end of July. According to it the supplies were scarce, but in spite of this it was questionable whether the value could be maintained, unless, indeed, a strong demand should set in from Europe. At the same time, however, it is expressly stated that the prospects are unfavourable, one district, for instance, which has hitherto produced 8000 kilos, will, it is said, yield barely 1000 kilos this year. Up to the end of June the exports amounted to 29 103 kilos, as compared with 44 140 kilos in the corresponding period of last year. For the present, as already mentioned, the position of the article is very firm, and although the existence of considerable stocks in Europe must be taken into account, we yet incline to the view that, at any rate in the next few months, higher prices will be the rule.

In our Autumn Report¹⁾ of last year we mentioned a Réunion geranium oil investigation in which the presence in the oil of α -terpineol among other bodies was determined. At the time we were unable to obtain this alcohol in a solid form, but since then we have succeeded in so enriching the corresponding fractions as to bring them to crystallising-point under prolonged cooling. The crystals, after recrystallisation, melted between 34 and 35°. Their specific rotatory power was very slight, *viz.*, $[\alpha]_D - 0^\circ 40'$ in a 10,36% alcoholic solution. As the active α -terpineols have a very high power of rotation, the substance here referred to is inactive α -terpineol, contaminated, moreover, by slight active admixtures.

The unprecedented manner in which essential oils are occasionally sophisticated is again illustrated by two samples of geranium oil which were submitted by a business-friend for our opinion. Examination showed that it was doubtful whether they contained any geranium oil at all! The following table gives the constants: —

	1.	2.	Réunion Oil	African Oil
d_{150}	0,9083	0,9087	0,888 to 0,896	0,892 to 0,904
α_D	+ 13° 24'	— 40° 40'	— 7° 30' to — 14°	— 6° 30' to — 12°
n_{D20}	1,47 957	1,48 910	1,462 to 1,468	1,464 to 1,472
Acid v.	1,8	0,9	3 to 12	1,5 to 12
Ester v.	33,1	11,0	50 to 78	34 to 70
Esterv. after acet.	203,7	143,7	208 to 233	203 to 232
Total geraniol	66,2%	44,3%	68 to 78%	66 to 77%
Solubility	3 vols. a. m. of 70% alcohol, the dilute sol. opalesces	insoluble	2 to 3 vol. a. m. of 70% alcohol, mostly with separ. of paraffin.	

¹⁾ Report October 1910, 69.

For purposes of comparison we have added to the above table the limits of value which we have observed in authentic geranium oils in the course of many years' experience. This comparison shows clearly to what (partly very considerable) extent the two samples deviate from genuine oils. The difference finds its greatest expression in the rotation, which makes it evident at once that both oils are heavily adulterated.

The odour of No. 1 oil, without further examination, pointed to the presence of gingergrass oil, and as the constants also agreed with those of that oil it is to be assumed that the bulk of the sample consisted of gingergrass oil. Possibly the oil may have been nothing else, but this could not be determined positively.

No. 2 oil had yet another admixture, further examination showing it to contain over 30% gurjun balsam oil¹⁾, which adulterant was left behind when the sample was treated with 80% alcohol, and was identified from its constants: $d_{15^{\circ}}$ 0,9199, $\alpha_D - 81^{\circ} 16'$, $n_{D20^{\circ}}$ 1,50. As already, it was doubtful whether this sample too, contained any geranium oil whatever.

Parry²⁾ also reports an interesting case of sophistication of geranium oil, namely with ethyl oxalate, which he discovered in several samples of Réunion (Bourbon) oil. The oils in question were suspected on account of their specific gravity, which was far too high (0,9093 to 0,9225) and their quite abnormally high ester-value (46 to 74%). In contradistinction to the behaviour of pure geranium oil, a crystalline substance (potassium oxalate) separated out in saponification. Parry isolated the acid and identified it as oxalic acid by the usual tests. Whether he has also identified the alcoholic constituent, and from it has found the ester to be ethyl oxalate, is not stated in his note.

Ginger Oil. Thanks to our excellent connections for the purchase of suitable raw material we have been able to secure sufficient quantities of ginger to satisfy even the extraordinarily heavy demand which, the high prices notwithstanding, has been experienced, especially from British consumers. There has been only very little change in the market-position of those varieties which are suitable for distilling, and it is therefore necessary to be prepared for high prices. Moreover, within the last few weeks a serious upward movement has set in in Cochin ginger.

Gingergrass Oil. There has been very little demand for this oil, chiefly for the reason that since the rise in palmarosa oil and the consequent introduction of our palmarosa oil substitute in the soap-industry, the latter preparation has been preferred, because it has not only a pure geranium-odour but is also considerably cheaper than gingergrass oil. It

¹⁾ We have already on a previous occasion referred to an adulteration of geranium oil with gurjun balsam oil. Report April 1908, 56.

²⁾ Perfum. and Essent. Oil Record 2 (1911), 83.

is therefore to be assumed that when this year's crop of gingergrass oil comes to market it will arouse very little interest indeed.

Oil of *Helichrysum angustifolium*. A sample of oil from *Helichrysum angustifolium*, D. C. (*H. italicum*, G. Don, N. O. Compositæ), obtained from Dalmatia¹⁾, gave the following constants: d_{150} 0,9005, n_{D200} 1,48209, acid v. 0,9, ester v. 61,1, sol. in about 9 vols. and more 90% alcohol. The colour of the oil was olive-green; its odour reminded somewhat of Roman chamomile; its opt. rot. could not be determined because of its intense colour. The present sample differs from oils of the same derivation previously described by us²⁾ by its ester value, which is decidedly lower.

Hop Oil. We have recently been compelled almost to double our prices for pure oil distilled from unsulphurated hops, cheap raw material suitable for distilling being unprocurable. Notwithstanding this fact our quality has been in such request that we have almost cleared our stock of oil from hops of the last season, which affords the clearest evidence of the unquestionable superiority of our distillate over the numerous cheap hop oils of commerce, most of which, merely by their odour, betray their derivation from sulphurated hops.

According to the communications of our informant the hop crop which is now in progress will fall short of that of 1910 by about 400 000 cwts. in round figures. This is due to the effect of the tropical heat and of the abnormal drought from which the plants suffered during the latter half of their growing period. The probable yield of the crop in the various countries concerned is as follows: —

	1911	1910	1909	1908
Germany	190 000 cwts.	395 000 cwts.	195 000 cwts.	535 000 cwts.
Austria-Hungary	175 000 "	325 000 "	170 000 "	400 000 "
England	330 000 "	320 000 "	200 000 "	475 000 "
America	370 000 "	365 000 "	400 000 "	425 000 "
Other countries .	135 000 "	175 000 "	90 000 "	250 000 "
World's Total:—	1 200 000 cwts.	1 580 000 cwts.	1 055 000 cwts.	2 085 000 cwts.

But although the estimate for 1911 is less by 25% than the yield of 1910, the fact must be taken into account, when forming an opinion of the probable course of prices, that very considerable quantities still remain available from last season, and that therefore for the present there is no need to anticipate a further serious upward movement.

¹⁾ See p. 63, footnote.

²⁾ Report October 1903, 76; April 1909, 57. In both these Reports, Sweet is mentioned as the author of the botanical name. The designation *Helichrysum angustifolium*, D. C. is in accordance with the Index Kewensis.

Hop-flower oil has as its principal constituent a sesquiterpene called humulene, which occurs also in oil from the leaf-buds of the black poplar (*Populus nigra*, L.). Deussen¹⁾ has recently discovered that this humulene is identical with *i*- α -caryophyllene. The author found the substance to occur in the fractions of hop oil boiling between 115 and 140° (8,5 mm.); after repeated fractionation it boiled between 118 and 119° (10 mm.). The nitrosate had m. p. 161°, which was not in the slightest degree depressed with *i*- α -caryophyllene nitrosate of the same m. p. The nitrolamine bases of the two compounds were also identical. Humulene nitrosochloride (m. p. 177°) suffered no depression of m. p. with *i*- α -caryophyllene nitrosochloride. Humulene also yielded a scanty proportion of a nitrosite which was not identical with β -caryophyllene nitrosite, and which may possibly be a derivative of *i*- α -caryophyllene, the nitrosite of which is as yet unknown. The scarcity of the nitrosite-yield may perhaps be due to the experimental conditions of the method of preparation not having been favourably chosen, or to the presence in hop oil of a small proportion of a second sesquiterpene hydrocarbon in addition to caryophyllene.

The aliphatic terpene of hop oil has also been investigated recently, Semmler and E. W. Mayer²⁾ having shown its identity with myrcene. The constants of the oil under examination were as follow: d_{20}^{20} 0,8781, n_D^{20} 1,4716; those of the myrcene-fraction: b. p. 62 to 63° (17 mm.), d_{20}^{20} 0,7937, n_D^{20} 1,4716. In order to identify the myrcene the authors prepared dibromo myrcene, dihydromyrcene tetrabromide and myrcenol.

Hyssop Oil has again been distilled by us from herb grown by ourselves, but the injurious effect of the heat and drought has also made itself felt in this article. We have only a limited stock and it will probably soon be necessary to raise the price.

Oil of *Inula viscosa*. From *Inula viscosa*, Ait. (*Cupularia viscosa*, Gren. et Godr.; *Pulicaria viscosa*, Koch; N. O. Compositæ), which they obtained from Algeria, Roure-Bertrand Fils³⁾ have distilled a pale brown oil, with an odour both of hyssop and of eucalyptus oils. The oil gave the following constants: d_{15}^{15} 0,9436, α — 24° 0', sol. in 1 vol. and more 80% alcohol, with separation of paraffin. With 10 vols. 70% alcohol the solution remained slightly turbid. About 70% of the oil were absorbed by a 50% resorcinol solution; hence the principal constituent of the oil appears to be cineol.

Some years ago, when engaged in distilling the same plant⁴⁾, we obtained an oil with quite different properties. It was viscous, of a dark brown colour, and even at ordinary temperature paraffin was separated

¹⁾ Journ. f. prakt. Chem. II. 83 (1911), 483.

²⁾ Berl. Berichte 44 (1911), 2009.

³⁾ Berichte von Roure-Bertrand Fils, April 1911, 23.

⁴⁾ Report October 1903, 76.

out from it. The sp. gr. was 1,006 at 25°. At the time we described the plant as *Inula viscosa*, Desfontaines.

Iva Oil. This oil has been very scarce for a considerable time, but during the past summer we have again succeeded in procuring a parcel of raw material of good quality. This has already been worked up, but the oil stands in at a higher price than previously.

Laurel Leaf Oil. An oil of laurel leaves prepared in Dalmatia¹⁾, which has been examined lately in our laboratory, gave the following constants: d_{150} 0,9268, α_D — 14°36', n_{D200} 1,46813, acid v. 0,5, ester v. 29,9, ester v. after acetylation 68,6, sol. in 2,5 vols. and more 70% alcohol. These constants agree with those of the German and French distillates.

A laurel oil derived from Syria has been examined by Roure-Bertrand Fils²⁾ and was found to behave as follows: d_{150} 0,9161, α_D — 14°20', soluble in 1 vol. and more of 80% alcohol.

Lavender Oil. Up to well within the month of July the lavender crop promised to yield an abundant return, all the climatic conditions for a healthy development of the plants having been fulfilled. Then, however, the tropical heat and drought which also visited other parts of Europe set in, suddenly changing the conditions for the worse. At the commencement of the distilling-period the yields were still good, but in proportion as the distilling approached its close, the flowers yielded poorer returns, part of the raw material being practically sun-burnt when brought to the stills. Hence the average yield fell below the normal, and, collating all the returns from the various districts, the total production this year may safely be estimated at only two-thirds of a good medium crop. In some districts, also, hail-storms had wrought great havoc, and destroyed the greater part of the lavender-plants. The districts of Mont Ventoux and Forcalquier in particular, which ordinarily produce the most lavender, had severely suffered from the unfavourable weather. Relatively the most favourable result was obtained in the region of Barrême and Digne and in the Northern part of the Department of the Maritime Alps, although there also the crop left something to be desired. Hence our Barrême works were able to take the utmost advantage of their favourable situation right in the centre of these districts. The labour question is becoming more difficult every year, wages being steadily on the increase, and the labouring-classes being with difficulty persuaded to keep from flocking into the towns, where they have a prospect of earning more money. Naturally this regrettable fact also tends in a not inconsiderable measure to affect the price of the product.

¹⁾ Comp. footnote p. 63. On laurel leaf oils of various origin see also Report April 1909, 60

²⁾ Berichte von Roure-Bertrand Fils, April 1911, 25.

The turnover at the fairs at Sault (Vaucluse), which are held on Wednesdays from the beginning of September, has so far been insignificant, because the growers demand from 25 to 30 frcs. per kilo for their oil, according to quality, and even those firms which usually attempt at the beginning of the buying-period to rush up the prices could not bring themselves to concede such figures. The fairs at Digne on September 2 and 9 also resulted in very little business, the high rates being generally insisted upon, and only a few small parcels of the better grades changed hands privately at from 28 to 29 frcs. Similar dulness prevailed at Apt. As the consumers are already beginning to show urgent need of supplying themselves, the growers will probably seize the opportunity to increase their requirements, and, if occasion should serve, to engineer a serious advance, and this the more readily because stocks from the previous season are no longer available.

The important problem remains what will be the attitude of buyers and sellers at the fairs at Luc-en-Diois on September 19 and at Sédron on September 21, that is to say in the Department of the Drôme. Unfortunately this Report goes to press before these dates.

Our Barrême works have worked full time day and night, and last year's output has even been exceeded, the total quantity distilled being 294500 kilos flowers. At Sault we distilled 86258 kilos, as against 85000 kilos in 1910. Accurate figures concerning the other places where we have caused lavender to be distilled are not available at present, but probably the total will only be slightly below that of 1910. As in previous seasons, the quality of our own distillate is unsurpassed; the first supplies which have arrived in Miltitz show the usual ester-content of over 50%.

A sample of lavender oil which was submitted to us for judgment had to be rejected, as a result of analytical examination, on account of its high specific gravity coupled with its low ester-content, the oil being moreover open to the suspicion of having had glycerol esters added to it. As the firm which had supplied the oil energetically disputed the possibility of its having been adulterated, and, on the other hand, insinuated that the chemist who had passed the judgment had been guilty of partizanship, we asked for, and procured, a large sample of the oil in question, as it was desirable directly to isolate any foreign ester which might be contained in it.

The analysis gave the following result: d_{15}^{20} 0,8994, $\alpha_D - 4^\circ 3'$, acid v. 0,5, ester v. 80,0, ester calc. as linalyl acetate 28%, soluble in 2,5 vols. a. m. 70% alcohol. No terpinyl acetate and esters of sparingly soluble acids could be detected; on the other hand, when the oil was tested for glycerol ester¹⁾ 0,7 cc. seminormal potash liquor was used up for 10 cc. of the

¹⁾ Report April 1911, 150.

aqueous filtrate, which fact pointed to the presence of the said ester. In order to separate it 900 g. oil was extracted three times with 900 cc. each time of water containing 5% alcohol, and of each of the aqueous filtrates 10 cc. was neutralised and saponified with seminormal potash liquor. The consumption was: No. 1 1,19 cc., No. 2 0,40 cc., No. 3 0,25 cc. seminormal potash liquor, hence the artificial ester which had been present in the oil had been removed, except for some small residue. The three aqueous solutions were evaporated to a small volume on the water-bath, and the residue was subjected to fractional distillation *in vacuo*. At 5 mm. pressure there passed over between 125 to 130° a few grams of a somewhat thick, yellowish liquid which was identified as glycerol ester by its properties ($d_{15^{\circ}}$ 1,1612; acid v. 4,9; ester v. 533,8; miscible with water and alcohol) and other characteristics¹⁾. As glycerol ester is not a natural constituent of lavender oil, or, in fact, of any other essential oil, its presence can only be accounted for as having been added intentionally.

The constants of the extracted lavender oil were as follow: $d_{15^{\circ}}$ 0,8970, acid v. 0, ester v. 76,5, corresponding to 26,8% linalyl acetate. This low ester content, taken in conjunction with the high specific gravity, warrants the conclusion that the oil had further been adulterated with spike oil or with some similar oil.

An article on lavender-growing which has appeared in a French technical Journal²⁾ reproduces in the main the statements on the same subject first published many years ago by Prof. Zacharewicz³⁾, of Avignon. We have referred to this matter in a previous Report⁴⁾.

A short paper by L. Lamothe⁵⁾ on lavender and its distillation also consists in part of a repetition of the same author's earlier and much more detailed statements issued in pamphlet-form⁶⁾; although on the present occasion Lamothe goes into closer detail on the subject of the distilling-practice. He proposes that the old stills should either be done away with altogether and replaced by stills of modern pattern, worked, perhaps, by steam, or modernised where this can be done without too great a cost, thus improving both the quantity and the quality of the output. Lamothe lays special stress upon the desirability of the lavender-flowers not being in direct contact with the bottom and the sides of the still, because, when they are, they are apt to get singed when there is not enough water in the still, and this may injuriously affect the quality of the distillate. He therefore recommends that the flowers should be

¹⁾ Report April 1911, 151.

²⁾ Parfum. moderne 4 (1911), 47.

³⁾ Culture de la lavande vraie. Bulletin mensuel du Syndicat Agricole Vaclusien 23 (1907), 230.

⁴⁾ Report April 1907, 62; October 1907, 58; April 1908, 65.

⁵⁾ Rev. de Grasse 54 (1911), No. 24.

⁶⁾ Lavande et Spic. A detailed abstract appeared in our Report November 1908 76.

placed in a cylindrical container of tinned copper or galvanised iron, perforated on all sides, and allowing a space of about one inch between the sides of the container and those of the still in which it is inserted, and of from 1 to 2 inches between the bottom of the container and the still. According to Lamothe, the same result might be achieved by so constructing the oven that the still is not exposed to the direct action of the flames, but only to that of the gases generated by the fire. For further particulars we refer to the original, but we desire to point out that in his proposals for improving the distilling-method, Lamothe has left the chief point out of account, or at any rate has laid insufficient stress upon it. This is that in the distilling-process the lavender flowers should not be directly immersed in boiling water, but should only be allowed to come into contact with the steam. This is most easily accomplished by inserting a perforated plate or bottom above the water in the still, and placing the flowers upon it. Obviously, it is also possible to suspend the container recommended by Lamothe in the still in a suitable manner. This method of distillation, to which C. von Rechenberg has applied the name of "Water-and-Steam Distillation"¹⁾ is the most suitable for itinerant stills and, especially in the case of lavender oil, is much more profitable than the ordinary water-distillation. The experience gained by us at Barrême and Sault in the distillation of lavender flowers has been related in detail in a previous Report²⁾.

The colour of lavender oil is yellowish, Lamothe's assertion that oil of good quality is almost colourless only holds good in exceptional cases.

Lemongrass Oil. In one of our earlier Reports³⁾ we described several lemongrass oils produced in the Jalpaiguri District of Northern India. Mr. J. H. Burkill of Calcutta, who sent us the samples of the oils in question at the time, has now briefly informed us in writing that this particular species of grass has been identified since then as *Cymbopogon pendulus*, Stapf. This information is of particular interest because up to the present only two grasses have been known to produce lemongrass oil⁴⁾, namely *C. flexuosus*, Stapf, which yields the Malabar oil, and *C. citratus*, Stapf, the parent-plant of the sparingly-soluble, so-called West Indian lemongrass oil. The oil from *C. coloratus*, Stapf, which is also one of the lemon grasses, has only lately become known, and is said to possess characteristics resembling those of a mixture of lemongrass and Java citronella oils⁵⁾.

Limette Oil. Another considerable parcel of hand-pressed West Indian oil has recently arrived for our account, and we have thus been able to

¹⁾ C. v. Rechenberg, *Theorie der Gewinnung und Trennung der ätherischen Öle durch Destillation*. Miltitz nr. Leipzig, 1910. p. 293.

²⁾ Report April 1907, 63.

³⁾ Report April 1910, 73.

⁴⁾ Report April 1907, 33.

⁵⁾ Report April 1911, 58.

reduce the price by a trifle. It so happens that in recent months the demand has been very brisk, probably, in the first place, because of the increased requirements of the aerated-water manufacturers. The terpene free variety has been specially preferred.

Linaloe Oil. Generally speaking, the position of Mexican linaloe oil has undergone no change, but occasionally the prices have been affected by the listlessness of the market and transactions of some importance could only be concluded by some sacrifice on the part of the sellers. The flatness of the market is due chiefly to the effect of the competition of the excellent Cayenne linaloe oil, which was usually obtainable at lower rates than the Mexican oil, while at the same time its intrinsic worth is undoubtedly greater. The output of this oil in Cayenne has lately assumed dimensions which must be pronounced unhealthy, for on every side complaints are rife that the manufacture does not pay. The attempts to unite the numerous small distillers into an association for the protection of their interests has miscarried owing to the opposition of a few wealthy firms, who in the end will probably hold the field, hence the future of this comparatively young industry in Cayenne does not appear to be particularly rosy.

Cayenne linaloe oil. While fractionating a considerable parcel of Cayenne linaloe oil, we succeeded in detecting in the first runnings, and in isolating therefrom, methylheptenol, a body discovered by us some years ago in Mexican linaloe oil¹⁾. The first runnings which contained the body had $d_{15} 0,8655$ and $\alpha_D - 11^\circ 40'$. The alcohol, which was isolated with phthalic ester, was identified by oxidising it into methylheptenone of which the semicarbazone melted at 137 to 138° .

Lovage Oil. What has been said under angelica root oil also applies to this oil. The crop of lovage must be described as a complete failure and the small supplies which are available to meet the requirements until next autumn are therefore, so to speak, worth their weight in gold. For the present the price has risen from 300 M to 500 M per kilo and the tendency is firm.

Mustard Oil. Our fears that the substitution, in the last edition of the German Pharmacopœia, of artificial mustard oil for the natural oil previously official would very seriously affect the consumption of the last-named article have been realised, and as it may be assumed that sooner or later the German example will be followed in foreign Pharmacopœias, it appears to be probable that the natural article is destined to disappear from commerce before very long. There is, in fact, no material difference in the action of the two oils, hence the question of quality can scarcely be adduced as an argument for the indispensability

¹⁾ Report November 1908, 85.

of the natural oil. We take this opportunity to call attention to the fact that the manufacture of artificial mustard oil from allyl alcohol has been one of our specialities for many years past, and that we are therefore thoroughly well equipped for the supply of this article. In the case of contracts of some importance we are in a position to make very favourable quotations, always assuming that there will be no advance in the cost of raw material in the near future. As we have already pointed out in earlier Reports, we cannot affect to deplore the sealing of the doom of natural mustard oil; in fact, in view of the unfair competition which for years has marred our pleasure in the sale of pure oil of our own distillation and made business in the article irksome, we hail the alteration with satisfaction as a fresh step towards the suppression of sophistication in our branch of business.

Myrtle Oil. To the enumeration of the constants of several myrtle oils of different origin published in a previous Report¹⁾ we are now able to add those of a Dalmatian distillate²⁾ recently examined in our laboratory. This oil possessed the following characteristics: $d_{15^{\circ}} 0,9254$, $n_D^{20} + 13^{\circ}20'$, $n_D^{20} 1,46694$, acid v. 1,0, ester v. 134,8, ester v. after acetyl. 186,7, sol. in 3,2 vols. and more 70% alcohol. The high ester-value of the oil is remarkable and the proportion of acetylisable constituents also is exceptionally high.

Neroli Oil. Our anticipation that the Société coopérative de production des propriétaires &c. would fix its prices for the new flowers at not less than 80 to 85 centimes, has not only been confirmed, but has even been surpassed by the fact that ultimately the price was increased to 85 to 90 centimes according to quantity. This, in view of the prospective crop, was certainly high enough, and its effect would naturally have been to increase considerably the cost-price of the new oil. During the gathering, rain and cold weather prevailed and unfavourably influenced the oil-yield, which did not reach the average percentage. The prices of neroli oil, which had gradually somewhat receded during the months preceding the crop, acquired increased firmness as a result of the above conditions, and a few transactions were even carried through at 500 fcs. per kilo. Owing to the high flower-price fixed by the Société coopérative, that Society has been compelled itself to take over and distil considerable quantities of flowers, and in view of the quietness which has prevailed in the neroli oil trade since June, it is probable that large quantities have accumulated in the Society's stores. For this reason we do not believe that prices will long be maintained.

There has been a further increase in the turnover of our Artificial Neroli "Schimmel & Co.". Wherever this exquisite product is submitted to a thorough practical test it will be found to represent not only a sub-

¹⁾ Report April 1909, 71.

²⁾ Comp. foot-note p. 63.

stitute for the natural oil fully equalling the latter in quality, but to surpass the natural oil by its greater lucrativeness, weight for weight. We cannot too often repeat that since the introduction and repeated improvement of our Artificial Neroli Oil, the employment of the natural article has become a luxury in the true sense of the word.

Roure-Bertrand Fils¹⁾ have received from Syria a neroli oil which behaved as follows: $d_{15} 0,8758$, $\alpha_D + 1^\circ 6'$, sap. v. $51,5 = 18^\circ$, linally acetate, soluble in 1 vol. and more 80% alcohol. When the oil was greatly diluted fluorescence ensued, with separation of paraffin.

Niaouli Oil. The oil from the leaves of *Melaleuca viridiflora*, Brongn. et Gris., known as niaouli oil, is recommended by Rallier du Batay²⁾ as a substitute for iodoform-ether and naphthol-camphor for injection in tuberculous ulcers, on the ground that its administration is less painful and attended by less danger than that of the other two remedies named. At first the dose is from 5 to 10 minims, but it is rapidly increased. At the commencement of the treatment a somewhat severe reaction is experienced, but the tuberculous ulcer is rapidly reduced and when the treatment is continued the pus-cavity is healed and cicatrises.

We abstract the following particulars from an article on the Niaouli tree³⁾ (*Melaleuca viridiflora*, Brongn. et Gris., N. O. Myrtaceæ), which has appeared in a French periodical: --- The niaouli tree is distributed plentifully throughout the whole island of New Caledonia. It resembles our birch tree in the pale colour of its bark, and it is said that in marshy districts it purifies the air, kills the mosquitoes and prevents the occurrence of fever. The wood, which is very durable, is a favourite material for shipbuilding, while from the bark a great variety of articles is manufactured. In addition to New Caledonia the niaouli tree also occurs in Annam where it is known to the natives by the name of *Cay-Tram*.

Nutmeg Oil. The want of nutmegs suitable for distillation is occasionally severely felt, but in the period under review there has been no lack of such qualities, and we have been able to offer this important article at unaltered cheap rates. Our output is considerable, and we are able to quote special rates for large parcels.

Oil from *Ocimum viride*. From the Imperial Institute in London we received some time ago a sample of oil which had been obtained from *Ocimum viride*, Willd. (N. O. Labiataë); a native of tropical West Africa. The oil had a thyme-like odour, was of a brown colour, and possessed the

¹⁾ Berichte von Roure-Bertrand Fils, April 1911, 26.

²⁾ Quoted from: Der Kinderarzt 22 (1911), 149.

³⁾ R. Koch, Parfum. moderne 4 (1911), 50.

following physical constants: $d_{15^{\circ}}$ 0,9338, $\alpha_D + 0^{\circ}$, $n_{D20^{\circ}}$ 1,50418. It was soluble in 4 vols. a. m. 70% alcohol, the dilute solution turning opalescent. Treatment with 5% alkali liquor gave a phenol-content of 52%, the phenol being identical with thymol.

A fuller examination of the oil of *Ocimum viride* was published some years ago by Goulding and Pelly¹⁾. The plant itself is of some interest in being a reputed prophylactic against mosquito-bites²⁾.

Oil of *Ænanthe crocata*. From hemlock-dropwort or dead-tongue (*Ænanthe crocata*, L.; N. O. Umbelliferæ) an exceedingly poisonous plant which is frequent in England, F. Tutin³⁾ has prepared an alcoholic extract which, when distilled with steam, yielded 0,1% (calc. on dry herb) of a pale-yellow essential oil with a somewhat unpleasant odour. The oil gave the following constants: $d_{15^{\circ}}$ 0,9381, $\alpha_D + 1^{\circ}16'$ in a 25 mm. tube. It boiled between 100 and 200° (100 mm.), the greater part passing over between 180 and 200°. Furfurol was found to occur in the oil.

Opopanax Oil. Newly-distilled oil is again in stock, and the price remains cheap, as before.

Origanum Oil, Cretan. From Dr. Giaconi, of Trieste, we received some-time ago, together with a series of other oil-samples⁴⁾, three origanum oils distilled by himself in the islands of Curzola and Lissa. In view of the great diversity of origanum species it is a matter of importance to know exactly what is the botanical origin of a sample, and Dr. Giaconi therefore, at our request, procured for us also a sample of the distilling-material, for which courtesy we here return him our best thanks. Dr. Giessler found that the distilling-material was derived from *Origanum hirtum*, Lk. *a. albiflorum*, Hassk. The table below enumerates the constants of the oils:

	$d_{15^{\circ}}$	α_D	$n_{D20^{\circ}}$	Phenols	Soluble in
1.	0,9400	$+ 0^{\circ}20' (?)$	1,50436	60%	2,8 vols. a. m. 70% alc.
2.	0,9275	$+ 0^{\circ}8' (?)$	1,50068	57%	1,3 vols. a. m. 80% alc.
3.	0,9231	$+ 0^{\circ}6' (?)$	1,49394	51%	1,5 vols. a. m. 80% alc.

¹⁾ Proceed. chem. Soc. **24** (1908), 63; Bull. Imp. Inst. **6** (1908), 209; Report November 1908, 89.

²⁾ Comp. Report April 1904, 13.

³⁾ Pharmaceutical Journ. **87** (1911), 296.

⁴⁾ In addition to the above mentioned origanum oils, Dr. Giaconi sent us samples of the following oils, distilled by himself: Oils of *Calamintha Nepeta* (24), *Helichrysum angustifolium* (54), and *Satureja cuneifolia* (109). Also oil of laurel leaves (56), myrtle (61), rosemary (78), sage (80), spike (85), wormwood (101), and oils of peppermint (69). The figures in () denote the pages at which these oils are described in the present Report.

Samples nos. 2 and 3 gave no clear solutions with 10 vols. 70% alcohol, and owing to the dark colour of the three samples it was not possible to determine their optical rotation with exactness. The phenols consisted entirely of thymol.

In connection with the above we may here state that origanum oils of which the phenols consisted exclusively or mainly of thymol have also repeatedly reached us of late from Syria, whereas previous shipments received from that source¹⁾ contained only carvacrol. We have not been able to find out the cause of this change in the constitution of the phenols, but it may perhaps be the case that different species of origanum are being distilled in Syria.

An origanum oil imported from Syria by Roure-Bertrand Fils²⁾ was found to possess the following properties: d_{150} 0,9309, $\alpha_D + 1^\circ 6'$, sol. in $1\frac{1}{5}$ vols. and more of 80% alcohol. When the straw-coloured oil was allowed to stand for a considerable time, a transparent body separated out from it.

This body may possibly consist of cedar camphor, the presence of which we detected some years ago in an origanum oil from Smyrna³⁾. The oil examined by us gave the following constants: d_{150} 0,9386, soluble in 2 to $2\frac{1}{2}$ vols. of 70% alcohol.

Orris Oil. Since April last the prices of this important article have remained unchanged and although, as will be seen from the subjoined report of our local correspondents, Florentine orris root will be available this year at a reduction of a few percent on the prices of 1910, this fact does not warrant the expectation of a reduction in the price of our two distillates. As we have already pointed out, the selling-prices of orris oil are still far below the quotations which would be justified on the basis of the previous cost-prices, and if by any means the oil-content of the current year's crop should have suffered through the exceptional drought, a further increase in the quotations will be unavoidable. In any case we do not hesitate to advise our friends to lay in a liberal supply at the rates now prevailing.

As usual, our correspondents have sent us a detailed report on the orris root market in 1911, and we quote their statements textually below: —

“Since our last report on Florentine orris root the price has been more or less stationary at the previous level of 85 *M* for sorts cif. Hamburg. It was not until quite recently that the market began to sag somewhat, as is often the case when the new crop comes to market, and to this state of things the considerably reduced demand in anticipation of future developments has contributed its share.

¹⁾ Report April 1907, 73.

²⁾ Berichte von Roure-Bertrand Fils, April 1911, 24.

³⁾ Report October 1906, 48.

At the end of February 1911 there was available . . . 290 tons
of which up to the present has been exported 200 "
leaving a stock of 90 tons.

Of this residue, however, a considerable part is required to cover previous sales for delivery. It is clear from the appearance of that portion of the new crop which has so far been brought to market, that it has suffered from the great drought. It is neither of such good appearance nor so compact as last year's. The total output of the crop is estimated at from 600 to 700 tons. If the prices should rise it is highly probable that the two-year old roots will also be collected. Crop estimates, however, especially in an article like orris root, the cultivation of which is distributed over innumerable small gardens, are difficult, and it is only when everything has been gathered that even approximately accurate data can be collected.

At the first orris root fair, which was recently held, holders asked a price equal to 83 *M* per 100 kilos cif. Hamburg, but this did not lead to business, because the buyers would not exceed the parity of 80 *M*, and as the holders were not disposed to give way, no business was transacted. Privately, however, a few sales were made outside the market at the basis of *M* 80 cif. Hamburg. It is difficult to foresee what course the prices will take in the near future, and much will depend upon the attitude of foreign buyers. In an article so sensitive as orris, and in view of the optimistic tendency of the dealers, a very slight cause is usually sufficient to drive prices upwards.

According to the quantity available for the coming season, which in all probability will be moderate, it is scarcely probable that lower prices can be hoped for. The annual exports of the last 9 years have been as follows: —

From September	1902	to	August	1903		840 tons
"	"	1903	"	"	1904	820 "
"	"	1904	"	"	1905	500 "
"	"	1905	"	"	1906	920 "
"	"	1906	"	"	1907	550 "
"	"	1907	"	"	1908	525 "
"	"	1908	"	"	1909	755 "
"	"	1909	"	"	1910	760 "
"	"	1910	"	"	1911	560 "
						Total 6230 tons

or on an average **about 690 tons** per season as compared with an average yield of the crop in the years 1903—10 of 650 tons."

The U. S. Consul in Florence has sent a detailed report to his Government on the cultivation of orris root in Upper Italy. We take the following passages from this communication¹⁾: —

The plant grows in different kinds of soil, but that best adapted to its growth is the stony mountain soil. This, however, must be scientifically prepared, so that the sub-soil will not remain too compact, for that would be disastrous to the growth of the plant in the summer months. The roots also grow well in a loose soil mixed with sand, but when raised in such

¹⁾ Daily Consular and Trade Report, 1st June 1911.

a soil they are less odorous and compact. Rich yellow soil is still less adapted to the culture, as in it the plants die quickly. Rich land near manure heaps produces a large quantity of plants, but the roots then are worth nothing: they possess little fragrance, and when dried shrivel up and become unsaleable. The altitude of the plantation is of little importance, though the best ground is usually found on hill-sides. Orris, however, also grows high up in the mountains, but snow and ice make the cultivation very difficult there, and in such high situations the root takes a few years more to reach its full growth. The best plan is to prepare the soil for orris root by spring seeding with some variety of leguminous plant, and then to plough it deeply. The best months for planting are August and September, but orris may be planted as late as the first half of October. As, however, the plant begins to grow immediately upon being placed in the ground, the first two months mentioned are the best time. The best method of planting is to begin at the bottom of the hill and make holes with a hoe about 16" apart. The soil should be well hoed in May and again in September, but irrigation is not beneficial to the plants, as the roots become less compact in moist soil and there is a dangerous tendency towards fermentation — a condition which is also frequently brought about by manuring. If the production of a large number of plants (for planting out) is desired, a system of fertilizing with rich soil can be adopted. The best fertilizer is the seed of *Lupinus albus*, which, after having been previously baked in an oven, is placed in small quantities round each plant at the September hoeing of the first year. If the field is to be replanted with orris root, the soil should be well fertilized, and grass, maize or some other crop grown upon it for 3 or 4 years previously. The gathering of the crop begins in the second half of June, and is carried out in the following manner: — Some of the gatherers hoe out as many entire plants as can be handled during the following day, because the plants dry quickly when exposed to sun and wind. The plants are taken to a shelter, where the bulbous part of the root is carefully detached, care being taken to leave enough runners attached to the plant to make it possible for it to grow again in the following year. The bulbous root is then scraped, cleaned, and washed in running water. This work is paid at the rate of 6 centesimi per kilo for root weighed after the washing-water has been dried off. The roots are dried in the sun, with provision for covering against rain. It is well to spread out the roots before sunrise, in order that they may receive the bleaching effect of the morning dew. After 8 days' exposure to a strong sun the roots can be packed and stored. Artificial drying in ovens or in any other manner injures the root and makes it less white. In drying the root loses about one-third of its weight. The yearly production in the province of Tuscany is about 1 320 000 lbs., and the principal growing districts are Bagno a Ripoli, Figlino Valdarno, Incisa Valdarno, Pelago, Pontassieve, Rignano sull'Arno, Reggello, Lam-

porocchio, San Casciano, Val di Pesa, Castelfiorentino, Casellina e Torri, Cantagallo, &c.

As a matter of special interest we may point out that recently orris root grown in Santa Catarina, Brazil, has been offered for sale. It is claimed for it that it possesses all the excellent characteristics of Florentine root. We hope, in our next Report, to be able to express an opinion whether or not this Brazilian orris represents an article which may be expected to compete seriously with the Florentine root.

Patchouli Oil. There has been no change in this article, in this sense that the advance in the price of the raw material during the last few months has failed to make any perceptible impression upon the value of patchouli oil; in other words, the selling prices of the oil continue to be below the true cost of production if calculated on the basis of the present quotations for leaves. Determined price-cutting on the part of some of the less important producers has made business very unsatisfactory, but on several occasions we have derived some satisfaction from being able to prove by chemical examination the inferiority of such "cheap" qualities.

Pennyroyal Oil. During the period under review there has been no alteration in the condition of complete neglect which has prevailed in this article for more than a year. The supply is still considerably in excess of the demand, and we do not think that there is any prospect of improvement within the near future. No fresh information is so far available concerning American pennyroyal oil.

Peppermint Oil, American. As early as the month of May our New York branch had acquired the certainty that at any rate no fall in prices was to be expected during the coming peppermint oil season. At that time the fields were still very backward, for the abnormal drought was injuriously affecting the development of the plants and in parts had actually destroyed the plantations, which had to be ploughed up. This unfavourable prospect naturally offered special inducements to the speculative elements, which, after first depressing the market to the utmost of their powers, soon afterwards obtained control of the greater part of the new crop, about $\frac{3}{4}$ ths of the entire output of 1911 being in their hands by the end of July. This alone was sufficient to cause an advance in the prices, and when it became furthermore evident that both as regards production and available stock the conditions this year were decidedly less favourable than in 1910, an upward movement in American peppermint oil set in, which we, with others, have been compelled to recognize in our selling prices, having previously, by suitable hints, given our customers an opportunity of cheaply covering their requirements.

According to the data collected by the expert who has been appointed by our New York house to represent our interests in the producing countries, the plantations and stocks of oil in the U. S. are as follows: —

I. Michigan and Indiana.

Localities	1910 acres	1911 this year's planting	1911 Total acres	Left in farmers' hands from 1910
a) Michigan:				
Van Buren Co.	1625	551	1578	300 lbs.
Cass "	1367	310	1380	2600 "
Saginaw "	1000	350	1250	— "
Allegan "	1065	656	1060	— "
Berrien "	434	370	634	5000 "
Eaton "	515	145	475	2300 "
St. Joe "	438	242	402	900 "
Kalamazoo "	280	193	330	500 "
Montcalm "	171	97	232	— "
Branch "	176	105	144	2600 "
Muskegon "	59	20	65	— "
Total	7130	3039	7550	14200 lbs.
b) Indiana:				
St. Joe Co. & neighbourhood	2441	1123	2891	—
La Grange Co.	925	361	1071	—
Noble "	100	100	200	—
Steuben "	80	20	100	—
Total	3546	1604	4262	—

It will be seen from the above that there are 1136 acres more under peppermint than in 1910, including an excess over 1910 of 693 acres of new plantations.

II. Wayne County, New York.

Whereas last autumn 56 acres of peppermint plantations could still be found, the area under cultivation is now reduced to 20½ acres, which at an average yield of 15 lbs. per acre would only yield a total of 307 lbs. of peppermint oil. These figures therefore confirm our view that the peppermint oil industry has ceased to exist in the State of New York. It is all the more peculiar, in view of this fact, that certain competing firms still continue to offer "Wayne Peppermint oil" as a speciality in any desired quantity.

The stocks of oil in farmers' hands at the end of May of this year total 23800 lbs., as compared with not less than 108600 lbs. available at the corresponding period of 1910, so that this year a total falling-off of 74800 lbs. of available oil has to be reckoned with. Besides this, sup-

plies in the hands of the Western traders are said to have been 6000 lbs. less than last year, so that altogether we start with a deficiency of over 80000 lbs. The extensions of the plantations in Michigan and Indiana referred to above are insufficient to equalize this deficiency. As there are numerous complaints of poor oil yields and the old stocks had been almost cleared at the commencement of the crop at the end of July, it is believed that not more than 225000 lbs. of oil will be available to meet the world's annual requirements of from 280000 to 300000 lbs., and a further advance of the market is therefore confidently anticipated. The quality of this season's oil is very good, as more care is being taken every year to keep the fields as free as possible from weeds, to the great gain of the pure peppermint aroma.

Peppermint Oil, Dalmatian. From Dr. Giaconi, of Trieste, we have received a dozen samples of peppermint oil distilled by himself from French peppermint cultivated in Dalmatia. Most of the oils had been prepared from the green herb; they were partly in the crude state and partly rectified. The crude oils possessed a peculiar subsidiary odour of pennyroyal which, however, is evidently removable by rectification, for it was no longer perceptible in the rectified samples, hence the latter might possibly find employment in perfumery and in the manufacture of liqueurs. The limit-values of the constants are given below: —

	Crude oils	Rectified oils
$d_{15^{\circ}}$	0,9074 to 0,9127	0,9094 to 0,9141
" D "	— $15^{\circ}45'$ to — $20^{\circ}58'$	— $11^{\circ}45'$ to — $18^{\circ}12'$
$n_{D20^{\circ}}$	1,46229 to 1,46684	1,46041 to 1,46783
Acid v.	0 to 1,9	0 to 1,0
Esterified menthol . . .	3,4 to 4,8 ^{0,0}	2,6 to 3,8 ^{0,0}
Total menthol	46,3 to 54,2 ^{0,0}	39,6 to 54,1 ^{0,0}
Solubility in 70% alc.	2,8 to 3,4 vols. a. m. Most of the samples became opalescent when further diluted.	2,8 to 3 vols. a. m. Only in one case did the diluted sol. show opalescence.

The above distillates differ from English and American oils in that some of them have a lower rotatory power, while a few are poorer in menthol. They approximate more closely, of course, to the French oil, to which we have referred frequently in our Reports¹⁾.

Peppermint Oil, English. Those of our friends who, following the suggestion made in our last Report, have supplied themselves plentifully with 1910 oil, will have no cause for regret, for even as early as the month of August we were compelled to raise our prices by 10 π per kilo, and at the commencement of September a further advance was necessary. The cost price of unadulterated crude Mitcham peppermint oil this year is 34/- to 35/- per lb., a fact which clearly shows that our selling prices are in

¹⁾ Report April 1905, 62; October 1906, 58; April 1909, 76.

every respect justified, and that offers of cheaper Mitcham peppermint oils cannot apply to qualities equal to that of ours. It is hardly necessary to add that the unfavourable result of the crop is due to the abnormal heat and drought of the summer.

H. J. Henderson¹⁾ reports that in England it has been shown by experiment that the oil-yield of peppermint plants grown in damp, shady places is much smaller than that of plants grown in the open field. The peppermint plants which were the subject of Henderson's experiment were grown on a river bank and distilled before flowering. They yielded 0,1% oil possessing the following constants: $d_{0,9046}$, $\alpha_D - 27^\circ$, combined menthol 3,9%, free menthol 55,3%, total menthol 59,2%. At the same time, Henderson distilled peppermint grown in the open on heavy loam. This yielded 0,409%: $d_{0,9065}$, $\alpha_D - 27,4^\circ$, combined menthol 5,57%, free menthol 55,78%, total menthol 61,35%. Plants grown in the open field on deep sandy loam only yielded 0,19% essential oil ($d_{0,9046}$; $\alpha_D - 28,2^\circ$; combined menthol 4,74%; free menthol 54,72%; total menthol 59,46%).

Peppermint Oil, Hungarian. K. Irk²⁾ has examined samples of Hungarian peppermint oils³⁾ and found them to possess the following properties: $d_{150} 0,90142$ to $0,9157$, $d_{200} 0,89705$ to $0,92$, $\alpha_{D200} - 26,51$ to $- 32,40^\circ$, $n_{D200} 1,4632$ to $1,4666$, sol. in 2 to 4 vols. 70%⁴⁾, in 1 to 2 vols. 80% and in 0,5 vol. 90% alcohol; ester content 10,098 to 16,26%, esterified menthol 7,97 to 12,82%, menthol 42,815 to 55,38%, total menthol 56,48 to 65,19%, menthone 7,379 to 13,21%.

Peppermint Oil, Italian. L. Bourdet⁵⁾ gives the following constants for two Italian peppermint oils produced at Pancalieri, near Turin: $d_{150} 0,915$, $\alpha_D - 22^\circ 56'$ to $26^\circ 51'$. The samples were soluble in 2,9 vols. 70% alcohol and in an equal vol. of 80% alcohol. Both oils solidified in a freezing-mixture, a property which had not previously been observed in the case of Italian oils⁶⁾.

Peppermint Oil, Japanese. The state of excitement in the Japanese peppermint oil and menthol markets which we reported in April has not continued very long, especially as certain firms made it their particular business to undersell the market with cheap menthol stocks which they held from previous seasons. We heard reports, for instance, of recrystallised menthol being quoted as low as 35 *M* per kilo at the same time when,

1) Chemist and Druggist **79** (1911), 216.

2) Kísérletügyi Közlemények **13** (1910), 4. From a reprint kindly sent to us.

3) Comp. Report April **1911**, 91.

4) With the exception of two samples.

5) Bull. Sciences pharmacol. **18** (1911), 392.

6) For previous data given by us on Italian peppermint oils, comp. Report October **1902**, 66; April **1903**, 59; November **1908**, 100.

in consonance with the true market value, we were obtaining 44 *M* per kilo for menthol of our own manufacture. The article was to be had practically at any price, but the demand left greatly to be desired, as the consumers had been taken aback by the differences in the selling prices. It was not until the beginning of June that the position commenced to clear up, for at that time the first reports of the present year's crop in Japan had come to hand, and although these reports differ considerably, they agree in forcecasting a normal crop in Bingo. It is true that at the time no reliable information had yet been received with regard to the crop in Hokkaido, which is well-known to be the principal producing centre, but in the absence of business even the approach of the new crop was sufficient to weaken the market. Only at the end of August was it possible to survey to some extent the probable results, and the surmise that the crop would be a normal one was then confirmed. In the middle of September our informant estimated the total crop at from 226,000 to 228,000 Kin, of which from 61,000 to 63,000 Kin, would be produced at Bingu Bichiu, and the rest in Hokkaido and Yamagata. The entire crop has suffered greatly this year, more particularly in Hokkaido, from unfavourable climatic conditions, the damage having mainly been caused by the extensive inundations. In Eastern Hokkaido rust fungus (*Uredo*) has made its appearance, with the result that it became necessary, in that locality, to cut the peppermint from 15 to 20 days earlier than usual, in order to obviate the total dying-off of the plants. Hence the estimated yield of 160,000 Kin is hardly likely to be reached. The present tendency of Japanese peppermint oils is very firm indeed. The upward movement in the prices of American oil, as was to be expected, has brought with it a fair enquiry, and within the past few weeks several large transactions for later shipment from Japan have taken place at increased prices.

The price of menthol also appears to have passed its lowest point, for according to the latest telegraphic reports from Japan, the market is beginning to become somewhat firmer.

In our last Report we described the interesting experiments made by Thoms¹⁾ in growing Japanese peppermint at Dahlem near Berlin.

During the present summer Thoms²⁾ has again distilled peppermint oil from the Japanese plant; the yield (0,893% calc. for the dry herb) being slightly less than in 1910³⁾. Cuttings of the Japanese peppermint plants have also been supplied to South Germany, German East Africa, and German S. W. Africa. The last-named cuttings in particular have succeeded

¹⁾ Report April 1911, 92.

²⁾ Apotheker Ztg. 26 (1911), 686.

³⁾ This does not agree with the statement in the previous communication [Berichte d. deutsch. pharm. Ges. 20 (1910), 424] according to which the 1910 yield was 0,535% (calc. for dried herb).

excellently. From the herb raised from them and sent to Berlin, Thoms has obtained 0,862% oil, calculated for the dry drug.

The table below gives the properties of the South African oil as well as of that distilled at Dahlem and of an oil distilled in Japan. The high menthol-content of the African product (84,83%) is worthy of attention.

	I	II	III
	Old Jap. oil (dist. in Japan)	Oil from herb grown in German S. W. Africa	Oil from herb grown at Dahlem (summer 1911)
d	0,9043 (18°)	0,9032 (22°)	0,8954 (22°)
α_D	— 36,25° (23°)	— 35° (24°)	— 34,75° (25,5°)
acid v.	4,05	2,99	4,01
ester v.	27,73	4,68	12,744
ester v. after acet.	289,5	304,8	283,25
esterified menthol	7,74%	1,302%	3,546%
free menthol . . .	72,77%	83,528%	75,271%
total menthol . .	80,51%	84,830%	78,817%
Sol. p.	cannot be determined	+ 20 to 20,5°	+ 14,5°

Peppermint Oil, Saxon. As was to be feared, the result of the peppermint crop in our Miltitz plantations has only been very scanty, for with the tropical heat of the last few months there was of course no chance of any normal development of the plants. As, moreover, hardly anything was left available of last year's crop, our supplies may now be described as practically cleared. The small quantity which has actually been distilled has barely sufficed sparingly to supply the wants of a few regular customers, who but for these supplies would have been painfully embarrassed.

Petitgrain Oil, Paraguay. This article, which is such a very useful one in all branches of perfumery, has suffered complete neglect during the past summer, and even the occasional rumours of impending advance in the price have been unable to impart even the slightest life to business. Our informants stubbornly prophesy that great scarcity will soon make itself felt, as the labour conditions in Paraguay are growing more and more unfavourable, and a number of plants have consequently already been compelled to close down.

A petitgrain oil received from Syria by Roure-Bertrand Fils¹⁾ possessed the following constants: d_{150} 0,8857, α_D — 3° 24', sap. v. 77,4 = 27,1% ester calc. as linalyl acetate, soluble in 1 $\frac{1}{4}$ vols and more 70% alcohol.

¹⁾ Berichte von Roure-Bertrand Fils, April 1911, 26.



Average still.



Interior of still-shed.

Distillation of Pine cone oil (*Abies pectinata*).

Pimento Oil. At times suitable material was only procurable with difficulty, and if notwithstanding this prices remained unchanged, this has entirely been due to the fact that we allowed no opportunity to pass of making advantageous purchases. The crop in Jamaica is said to be belated this year, and reports from the island also state that owing to the drought an insufficient output must be expected. It is therefore probable that in the course of the next few months the quotations will rise.

Pine Needle Oils. We have received abundant fresh supplies of Siberian pine needle oil, a variety of which the sale is still increasing, but for these arrivals we have had to pay higher prices, as distilling is said to be unremunerative under the price-conditions formerly prevailing. We have nevertheless been able to content ourselves with a modest rise in our quotations, and we merely desire to point out here that care is desirable in purchasing Siberian pine needle oil, as the article is frequently adulterated with pine tar oil. The oil is used for so many different purposes that it may be described as one of the most popular adjuncts in the preparation of all kinds of technical products. Pine needle oils from *Abies alba* and *Pinus montana* (*Pinus pumilio*) have been obtainable in any desired quantity, and no price-fluctuations of any sort have occurred in these oils. On the other hand the stocks of oil from cones of *Abies alba* were drawing to an end early in the summer and prices became firmer. We have again made arrangements for securing considerable supplies of this season's distillation, which commenced in the month of September, but for these supplies we have been compelled to pay higher prices, as otherwise, it was said, the cone-collectors would have been unwilling to continue their dangerous and difficult occupation. This season, for the first time for many years, Switzerland has again entered the field in the supply of this oil, and we have therefore been able to draw a portion of our requirements from that country. In the Black Forest and in Thuringia fair quantities of oil from cones of *Abies alba* are also prepared. The demand is very animated indeed, and prices will therefore presumably keep at their present level.

By the courtesy of a business-friend in Berne we are enabled to give in the present Report a few plates illustrative of the preparation of oil from cones of *Abies pectinata*. The frontispiece shows a collector known as a *Brecher* (beater), whose business it is to climb the highest tops of the trees, where he picks and throws down the cones. The boys on either side of the beater are the *Leser* (gatherers) who collect the cones from the ground and pile them up in a shady place. The three other illustrations depict distilling-plant and a "*Brennhütte*" (still-shed). In one of them a woman is seen breaking up the cones.

Pine needle Oil from *Pinus pumilio*. In the oil of the needles from *Pinus pumilio* ("Latschenkieferöl") E. Böcker and A. Hahn¹⁾ have discovered some new oxygenated bodies. The authors examined an oil which had been freed from terpenes and sesquiterpenes (b. p. 85 to 178°; 13 mm.) which they split up into several fractions. A fraction boiling between 148 and 160° (α_D —14°15'; sap. v. 53) yielded a solid bisulphite compound, from which a liquid with a faint balsamic odour, possessing the elementary formula $C_{15}H_{26}O$ was regenerated. This body is probably an aldehyde, for with magenta-sulphurous acid a red coloration ensued. Its behaviour towards bromo-glacial acetic acid showed that the compound probably contained a double bond.

From a fraction boiling between 127 and 148° (13 mm.) the authors obtained a bisulphite compound which was extremely difficult to split up. In the course of the experiment it yielded a lævorotatory body $C_{15}H_{24}O$, containing two double bonds. This body is probably of the nature of a ketone.

Finally, a fraction boiling between 87 and 95° (14 mm.) and possessing the following constants: d_{150} 0,9288, α_D —18°15', sap. v. 65, was treated with sodium bisulphite, with the result that a highly volatile oil possessing the peculiar aroma of pumilio pine needle oil was liberated. This interesting body possesses the following properties: b. p. 216 to 217° (754 mm.), d_{150} 0,9314, d_{200} 0,9288, α_D —15°0', n_D 1,46459, and has the formula $C_8H_{14}O$. In view of its great density and high b. p. the authors regard it as probable that the new compound is of a cyclic character. It neither reacted with magenta-sulphurous acid nor with ammoniacal silver-solution; with permanganate of potassium it yielded a mixture of two acids; hence the body appears to be a ketone. The authors have given it the name of *pumilone*. Pumilone is a saturated substance, and yields a semicarbazone, m. p. 116 to 117°. It only occurs in the original oil in small proportions, about 1 to 2%.

Rose Oil, Bulgarian. Most persons interested in the course of the rose oil market have probably suffered severe disappointments this year. In the month of April the prospects were the most favourable imaginable and everybody was trying to get rid of his supplies as quickly as possible. We even heard it said that some of the more important Bulgarian traders at that time entered into contracts for delivery of the present year's oil at low prices. But at the end of May it suddenly became clear that the crop would fall considerably behind that of the previous year owing to the want of rain, and partly also to the serious damage done by insects.

In the producing districts the prices for new oil started at about 1300 frcs. per kilo, and, supported by the fact that no 1910 oil remained available on the spot, they rapidly advanced to their present figure of about 2000 frcs. This quotation, too, may be exceeded before long, for

¹⁾ Journ. f. prakt. Chem. II. 83 (1911), 489.

almost all exporters find themselves compelled to buy, and whether they like it or not, consumers will probably be compelled to concede the high rates. Nevertheless offers are current, especially in Paris and in London, at the approximate parity of 1000 to 1300 frcs. per kilo, showing that adulteration continues to be freely practised and that there is still no lack of buyers who place confidence in the fantastic recommendations of certain unreliable firms in view of the so-called "cheapness" of the offers. In selling Bulgarian rose oil we for our part will content ourselves with the most moderate profit, in order to make the unpleasant conditions prevailing this year at any rate a little less irksome for our customers.

According to a report from the German Consulate at Sofia dated 6th August, the rose harvest in Bulgaria has yielded an average of 1500 to 2000 kilos of flowers per hectare (from 12 to 16 cwts. per acre). In the division of Philippopolis (districts of Karlovo, Philippopolis, Pechtira and Panagurichte), which contains about 3987 hectares of rose gardens, it is estimated that the yield per hectare will be about 500 kilos in excess of that of last year. On the other hand, in the division of Stara-Zagora (districts of Kazanlik, Tschirpan, Stara- and Nova-Zagora), the yield of flowers has been smaller than it was last year. The quantity of rose oil distilled in Kazanlik this year is estimated at 157 000 to 158 000 muskals (one kilo = 208 muskals), as compared with about 200 000 muskals the year before. On the other hand, this year from 13 to 15 kilos of rose flowers have been sufficient to produce one muskal of oil, whereas in 1910 from 18 to 19 kilos were required. At the time of gathering the price of the flowers was 0.45 frc. per kilo.

Our Bulgarian informant has placed at our disposal the comparative tables of production according to districts, which are reproduced on pages 76 and 77 of the present Report.

Rose Oil, German. Although we have reason for serious complaint this year at the failure, owing to the great heat, of all the crops cultivated by us, it is nevertheless somewhat surprising that our crop of roses has been almost completely destroyed this season by unexpected cold. The buds set very satisfactorily in the month of May, and the appearance of the bushes warranted the highest hopes, when in the night from the 3rd to the 4th June the thermometer fell to -3° , and this single night-frost sufficed to destroy the greater part of the buds. As a result of this disaster we have this year distilled no rose oil whatever, but have used what remained of flowers chiefly for the purpose of making the extract, which, as is well known, is indispensable in the preparation of our new and successful speciality "Red Rose, Schimmel & Co." (see page 115).

Our remaining stock of German rose oil is limited to a few trifles carried over from the 1910 crop, which will no doubt be snapped up in the twinkling of an eye.

Production of pure Rose oil, arranged according to localities.
Crops 1910 and 1911.

Locality	1910 Kilos	1911 Kilos	Locality	1910 Kilos	1911 Kilos
District of Kazanlik.			District of Karlovo.		
Kazanlik	70	50	Karlovo	100	70
Alexandrovo	70	60	Adjar	100	85
Armaganovo	5	4	Arapovo	10	6
Achiklii	20	15	Begovo	6	4
Bahaslii	3	2	Bogas	30	20
Bitcherlii	2	2	Voinagovo	40	35
Gabarevo	30	20	Guilleré	25	16
Goliamo Sélo	70	50	Gornio Kusseleré	70	50
Gornio Sophylaré	25	30	Gornio Omarobas	10	6
Gornio Sahrane	5	3	Davadjovo	3	2
Gussovo	5	3	Derelie	60	45
Doïmouchlari	20	16	Dolnio Omarobas	50	36
Dolnio Sahrane	15	12	Dougandjii	3	2
Dolnio Sophylari	4	3	Mintichlii	5	4
Enina	105	70	Dabeni	35	16
Emichléri	3	2	Aiganovo	25	18
Elhovo	50	30	Ahiévo	15	10
Ekanlii	30	18	Kara Sarlii	25	15
Karaguitlii	25	15	Kalofer	50	35
Kazalatchderé	30	20	Klissoura	120	80
Kozloudja	25	10	Kotchmalaré	35	18
Kachlata	10	5	Achiklaré	15	10
Lahanlii	20	12	Madjaré	4	3
Malko Sélo	12	5	Mitirisovo	25	16
Maglige	85	50	Michiltzi	20	15
Nova Mahala	2	1	Mratchénik	45	33
Orosovo	25	15	Ortchilaré	40	35
Pavel Bagnia	40	25	Rahmanlaré	120	75
Ragina	20	10	Sindjirlii	12	8
Sequeretchevo	15	5	Slatina	30	24
Simitleri	25	15	Sopot	35	25
Slivito	4	2	Tekiá	20	18
Seltzé	3	2	Himitlii	4	2
Tarnitchané	25	18	Hissar	3	1½
Touria	30	16	Hissar Kusseleré	30	24
Tchanaktchii	12	5	Tchoukourlii	10	7
Toulovo	20	10	Kourtovo	15	9
Tscherganovo	3	2			
Hassate	15	9			
Himitlii	25	15			
Chipca	100	70			
Cheynovo	50	35			
Urenlii	13	6			
Total	1166	768			
			District of Plovdiv.		
			Babek	10	8
			Bresovo	8	6
			Carry forward:	18	14
			Total	1245	878½

Locality	1910 Kilos	1911 Kilos	Locality	1910 Kilos	1911 Kilos
Carried forward:	18	14	District of Tchirpan.		
Demirdjileri	2	1 ¹ / ₂	Alagun	15	12
Panitcheri	15	12	Baldjilaré	1	1
Aïreni	10	7	Goliamo Derelie	4	3
Rahmalii	120	85	Enicher	10	8
Staro Novo Selo	60	42	Echevren	10	7
Oustina	1	— ¹ / ₂	Kalfa	2	1 ¹ / ₂
Total	226	162	Kolatchevo	5	3 ¹ / ₂
Distr. of Nova-Zagora.			Sadaklii	20	16
Balabanli	8	6	Sakarlii	5	4
Bosagatch	3	2	Tchehlaré	30	22
Djoumalii	1	— ¹ / ₂	Mahmoutlare	6	4
Zapalnia	12	6	Hadjiolare	3	2
Kispetlii	5	3	Total	111	84
Kriva Kroucha	4	2	District of Pechtera.		
Smavli	2	1	Pechtera	5	4
Nikolaevo	5	3	Bratzigovo	46	35
Tvarditza	30	20	Bega	1	1
Dolnio Tschanaktchii	12	8	Kozarsko	16	12
Kozosmadé	12	10	Kritchim	2	1 ¹ / ₂
Hainito	12	10	Tchanaktchievo	5	3 ¹ / ₂
Konaré	30	20	Total	75	57
Total	136	91¹/₂	District Pazardjik	20	14
Distr. of Stara-Zagora.			„ Panagurichté	4	2 ¹ / ₂
Stara-Zagora	4	3	Recapitulation.		
Ada Tepé	10	8	Distr. of Kazanlik	1166	768
Arnaoutito	4	4	„ „ Karlovo	1245	878 ¹ / ₂
Beltchevo	1	1	„ „ Plovdiv	226	162
Dalboki	45	35	„ „ Nova-Zagora	136	91 ¹ / ₂
Zmeevo	4	3	„ „ Stara-Zagora	165	124
Kazanka	40	30	„ „ Tchirpan	111	84
Kolena	10	6	„ „ Pechtera	75	57
Nova Mahala	5	3	„ „ Pazardjik	20	14
Oriachovitza	20	16	„ „ Panagurichté	4	2 ¹ / ₂
Hamsalari	7	4	Total	3148	2181¹/₂
Hrichteni	15	11			
Total	165	124			

Two other reports which have reached us give the total production of the present year as follows: —

A: 2405,800 kilos,

B: 2581,750 „ .

The actual result of the present year's crop may probably be fairly accurately estimated by taking the mean of these figures.

Rosemary Oil. The supplies of last year's oil having been entirely cleared, very high prices are momentarily asked for French oil, but in view of the competition of the cheap Spanish oils it is improbable that these rates can be maintained. Dalmatian rosemary oil, of which the distillation has just been concluded, appears to have a slightly lower tendency in view of the restricted demand, but for the present nothing definite can be said on this head.

Three samples of guaranteed pure rosemary oils distilled in the island of Lissa (Dalmatia)¹⁾ gave the following constants:

	d_{150}	α_D	α_D of the first 10%	sap. v.	soluble in
1.	0,8941	+ 0° 44'	+ 2° 40'	19,3	0,5 to 0,8 vols. a. m. 90% alcohol.
2.	0,8945	+ 0° 43'	+ 2° 28'	18,5	
3.	0,9003	+ 1° 27'	+ 1° 14'	not determined	

Samples Nos. 1 and 2 in particular gave no clear solutions with 10 vols. 80% alcohol. This fact, as well as the exceptionally low sp. gr. of these two oils, is perhaps due to their having been distilled in May, at the beginning of the season, from green herb, which made them specially rich in terpenes.

P. Jeancard and C. Satie²⁾ have published a comprehensive essay on rosemary oil. They base their statements upon their own experiences of the article gathered between the years 1906 and 1910, and arrive at the conclusion that rosemary oil should be required to behave as follows: d_{150} 0,900 to 0,920, α_D + 0° to + 12°. Total borneol 9 to 18%; solubility in 85% alcohol = 0,5 to 1 and in 90% alcohol = 0,1 to 0,5. According to the experience of the authors, not all rosemary oils are soluble in 80% alcohol. The bornylacetate content varies from 1,7 to 5,1%.

Jeancard and Satie also deal at length with the question whether the want of solubility of certain Spanish rosemary oils justifies the conclusion that they have been adulterated with turpentine oil, and whether this point can be determined by analysis, but they do not arrive at any positive conclusion. In dealing with this matter they also refer to the distilling-method recommended by us. This method consists in distilling off 5 cc. oil from a Ladenburg flask of 50 cc. capacity and testing the rotatory

¹⁾ Comp. foot-note p. 63.

²⁾ Americ. Perfumer 6 (1911), 6; Rev. gén. de Chim. 14 (1911), 125. From a reprint kindly sent to us.

power of the distillate. Jeancard and Satie maintain that we ourselves have declared this test to be illusory on the ground that the result depended entirely upon the size of the Ladenburg flask. With regard to this we feel bound to state that we have never expressed such an opinion of our distilling-method, and that the authors have evidently misunderstood something that has been said by us. It goes without saying that the test must always be carried out under identical experimental conditions if it is desired to obtain comparable results, and for that reason, when publishing the method¹⁾, we carefully laid down the dimensions of the Ladenburg flask, because of course this is a point of special importance. In our own practice the method in question has often rendered excellent service, and it is still in daily use in our laboratories, which is the best possible proof that we do not regard it as illusory. It is true, however, that, basing ourselves upon the experience gained by us in the course of years, we have stated that a lævorotation of the first 10% of the distillate does not necessarily imply that the rosemary oil showing such a rotation is adulterated²⁾, but it will be quite easy to judge every case of this kind upon its own merits, bearing in mind the other properties of the sample.

Rue Oil. The genus *Ruta* comprises about 50 species of which the following four occur in France, namely: *Ruta montana*, L. (*R. tenuifolia*, Desf.), *R. angustifolia*, Pers. (*R. chalepensis*, L.), *R. bracteosa*, D. C. and the common garden rue, *Ruta graveolens*, L. The same species, with the exception of garden rue, also occur in Algeria. As reported by F. Jadin³⁾, these *Ruta* species are easily distinguishable from each other by examination of their anatomic structure, sections of the stalks in particular showing characteristic features.

The oil of *Ruta montana*, which is cultivated in Algeria, is usually known as "essence figeable". It contains about 90% methylnonylketone and solidifies completely at $+10^{\circ}$: $d_{15^{\circ}}$ 0,8307, $\alpha_D + 0^{\circ} 42'$; soluble in $2\frac{1}{4}$ vols. and more of 70% alcohol.

The properties of the oil of *Ruta bracteosa*, which is also cultivated in Algeria, are totally different. The oil examined by Jadin was obtained from the flowering plant; it contained about 90% ketones, but did not solidify even at -15° : $d_{15^{\circ}}$ 0,8410, $\alpha_D - 4^{\circ} 12'$, sol. in 2 vols. of 70% alcohol, when more is added the solution acquires a blue fluorescence, while paraffin is separated out from it. The constants of this oil are almost the same as those of an Algerian oil of rue which was examined by v. Soden and Henle⁴⁾; hence the two products are probably identical.

¹⁾ Report October 1898, 41. Also compare Gildemeister and Hoffmann, *Die ätherischen Öle*, 2nd Ed. I. 585.

²⁾ Report October 1904, 82.

³⁾ Berichte von Roure-Bertrand Fils, April 1911, 11.

⁴⁾ Pharm. Ztg. 46 (1901), 277; Report October 1901, 47.

The fluorescence to which reference is made above as showing itself when the oil is diluted with alcohol is perhaps caused by the methylester of methylantranilic acid¹⁾.

Sage Oil. The extent to which the character of oils is influenced by the season and the conditions of the distilling-material is shown by two authentic Dalmatian sage oils which reached us some little time ago²⁾. One of the samples, which had been distilled in August from dried sage, showed normal properties in every respect ($d_{15^{\circ}}$ 0,9165; $\alpha_D + 25^{\circ}$; $n_{D20^{\circ}}$ 1,45871; acid v. 1,0; ester v. 9,3). The sp. gr. of the other, prepared in May from the green herb, was lower than is otherwise the case with Dalmatian sage oils. As a rule the sp. gr. of such oils ranges from 0,915 to 0,930; in the case under notice it was only 0,911. It was obvious that this oil was rich in terpenes, and this was confirmed by the fact that it required 1,1 vols. 80% alcohol for solution, whereas the oil distilled in August was soluble in 4 vols. 70% alcohol. The other constants of the oil were normal: $\alpha_D + 20^{\circ}22'$, acid v. 1,0, ester v. 10,3.

A sage oil which was imported from Syria by Roure-Bertrand Fils³⁾ gave the following constants: $d_{15^{\circ}}$ 0,9843, $\alpha_D - 6^{\circ}8'$, soluble in 1,5 vols. and more 70% alcohol and in its own vol. and more 80% alcohol.

Sandalwood Oil, East Indian. Business in this important article has continued to be exceedingly brisk during the summer-months, and it has therefore been unnecessary to interrupt our manufacture, in spite of the fact that our gigantic distilling plant, which we have already described on a previous occasion, has a capacity which must appear almost incredible to most persons interested in the article. The principal advantage of this installation is that we are able to work up the wood immediately upon its arrival, and thus to obviate as far as possible those losses which are invariably connected with prolonged storage of the material. Generally speaking prices have remained unchanged. The demand for our quality with a guaranteed santalol-content of 94% has naturally been exceedingly strong, and we have had the satisfaction of gaining large numbers of new and important customers. As regards the prospects, only this much can be said with any degree of definiteness at present, that there is scarcely any possibility of a fall in the prices within the next few months. It is true that only preliminary reports are as yet available concerning the forthcoming sandalwood auctions in Mysore, but it is certain that again no efforts will be spared to make them as profitable as possible for the Government.

¹⁾ Report October 1901, 47.

²⁾ Comp. foot-note p. 63.

³⁾ Berichte von Roure-Bertrand Fils, April 1911, 25.

The annual auction-sales of sandalwood of the Mysore State will be held at the undermentioned places, on the dates specified against each, by the Deputy Commissioner and the Forest Officer of the district.

Serial No.	District	Kotie	Date of Sale	Approximate quantity in Tons
1	Shimoga	Tirthahalli	13 th Nov. 1911	225
2	id.	Sagar	16 th " "	100
3	id.	Shimoga	20 th " "	475
4	Kadur	Tarikere	23 rd " "	250
5	id.	Chickmagalur	27 th " "	250
6	Hassan	Hassan	30 th " "	150
7	Bangalore	Bangalore	4 th Dec. "	120
8	Mysore	Seringapatam	13 th " "	250
9	id.	Hunsur	16 th " "	500
Total Tons				2320

Details as to quantities and lots of sandalwood to be exposed for sale as above in each kotie together with the terms of sale will be published as usual about the end of October 1911.

Any wood that may remain unsold at any kotie will not again be put for auction, but will be sold, if found necessary, by tenders after the conclusion of the auction-sales.

A sample of sandalwood oil which was sent to us from Hamburg was most impudently adulterated. Its very appearance was suspect, the oil being studded with sparkling crystals, which became so plentiful under cooling as to cause the whole sample to solidify into a jelly-like mass. The constants were: d_{150} 1,0026, α_D $-7^\circ 24'$, n_{D200} 1,51620, sap. v. 63,1. The spec. grav., the index of refraction, and especially the saponification value were much too high for sandalwood oil, while on the other hand the optical rotation was less than half of what it should have been. All these data, together with the insolubility of the oil in 70% alcohol, seemed to indicate that the sample did not represent sandalwood oil at all. When distilled carefully under 5 mm. pressure further abnormalities presented themselves.

			α_D	n_{D200}	Sap. v.
1.	120 to 132°	13,1%	-17°	1,50602	—
2.	132 to 135°	18,4%	$-8^\circ 20'$	—	—
3.	135 to 138°	33,1%	$-3^\circ 52'$	—	29,4
4.	Residue	35,4%	$-6^\circ 42'$	1,51770	153,0

Part of the first two fractions solidified completely owing to a solid body being separated out, which upon further examination was identified as guajol, a sesquiterpene alcohol possessing the formula $C_{15}H_{26}O$. The quantity of this substance was large enough to admit of its isolation and recrystallisation. Its m. p. was then determined as between 91 and 92° , the spec. rot. in 8% alcoholic solution was $[\alpha]_D - 29,1^{\circ}$ and when warmed with concentrated formic acid water was eliminated. Guajol not being a constituent of East Indian sandalwood oil, its presence could only have been caused by the deliberate and fraudulent addition of guajac-wood oil, which costs about one-third of the price of sandalwood oil. But this adulteration by itself would not explain the abnormally high specific gravity and the high saponification value of the oil under examination, nor of the distillation residue. A further sophistication was required to explain these, and that this sophistication consisted of a high-boiling benzoic ester was proved by the isolation, from the saponification liquors of the distillation-residue, of benzoic acid, m. p. 122° . This acid, too, is not to be found in normal sandalwood oil and can only have been added to the sample by some fraudulent manipulation. The added ester was probably benzyl benzoate.

Sandalwood Oil, Guiana. P. Jeancard and C. Satie¹⁾ have distilled an essential oil from sandalwood which came from Guiana, but as to the botanical origin of which nothing could be identified. The analytical constants of the oil were as follow: d_{150} 0,9630 to 1,0122, $\alpha + 0^{\circ}30'$ to -6° , sap. v. 13 to 65, sap. v. after acetylation 65 to 117, sol. in 1,5 to 12 vols. 75% and in 0,8 to 1,1 vols. 80% alcohol. The oil contained from 59 to 80% of a fraction boiling between 155 and 160° (20 mm.) (d_{260} 1,024 to 1,037; $\alpha - 4^{\circ}20'$ to -6° ; sol. in 1,8 vols. 70% alcohol).

The properties of the oil depend in a large measure upon the nature of the raw material, for which reasons samples were distilled from branches (I), trunks (II) and logs (III) from which the bark had been removed. The constants of the oils distilled from these several lots were:—

	I	II	III
d_{150}	0,9665	0,9806	0,9968
α	$-6^{\circ}16'$	0	$+0^{\circ}30'$
Solubility in 85% alc. . .	0,4	0,4	0,3
" " 80% " . .	1	1	0,9
" " 75% " . .	1,7	10,8	20
Sap. v.	44,1	46,9	13,3
Ester v. after acetylation	92,4	96,6	65,8
Total of fraction boiling } at 155 to 160° (20 mm.) }	44%	51,4%	49,8%
Total of fraction boiling } at 160 to 165° (20 mm.) }	9,4%	12,6%	24%

¹⁾ Perfum. and Essent. Oil Record 2 (1911), 70.

The fraction boiling between 155 and 160° contained a body (b. p. 155 to 159° (20 mm.); d_{230} 1,0378; α — 6°; sol. in 1,6 vol. 70%, in 2,7 vol. 65% and in 6,5 vol. 60% alcohol), which Jeancard and Satie name *marionol*. Marionol is probably a tertiary alcohol. It cannot be acetylated in the usual manner, when heated with acetic anhydride in xylene solution the saponification value after 1 hour's boiling was 147, after 3 hours', 168 and after 5 hours', 189.

We ourselves distilled oil from Guiana sandalwood in the year 1910. At the time Dr. Giessler, Curator to the Botanical Institute of the University of Leipzig, informed us that the wood belonged to the N. O. Lauraceæ, and was probably derived from three species of the Genus *Acrodictidium* or *Ocotea*. The oils distilled by us gave the following constants:

	I	II	III
Yield	3,28%	2,48%	4,14%
d_{150}	1,0036	0,9570	0,9990
α_D	— 4° 26'	— 0° 46'	— 0° 44'
Acid v.	1,9	3,7	0,9
Ester v.	10,6	68,8	2,4
Ester v. after acet.	72,9	113,3	54,1
Solubility in 80% alc. . .	1 Vol. a.m.	2 Vol. a.m.	1 Vol. a.m.

Sandalwood Oil, West Indian. Uninterrupted supplies of considerable quantities of wood have enabled us to distil very large quantities of oil, and as we have also been able to secure new and considerable parcels for future delivery, it is unlikely that the want of raw material which has so often made itself felt in the past will recur for some considerable time to come. We are in a position to supply West Indian sandalwood oil in any required quantity, and are prepared to make favourable special quotations for large contracts.

Sasanqua Oil. From the young leaves of *Thea Sasanqua* (N. O. *Theaceæ*), a tree which is indigenous in Japan, H. Kimura¹⁾ has distilled a brown or violet-coloured oil (yield 0,4 to 1,0% calc. on green herb) of a sweetish odour, possessing the following properties: d_{210} 1,0611, α_D + 0. The oil contained about 97% eugenol (m. p. of the benzoyl compound 69 to 70°) and further, an ester of an alcohol with a pleasant rose-like odour and traces of a substance which reacted with bisulphite.

Sassafras Oil. A brisk turnover has kept prices in the United States at a high level during the past few months, but the offers from the growing districts are reported to have been rather more liberal lately. As yet, however, prices have not given way enough to enable us to hold out expectations of an early considerable reduction in our October quotations. We have not received any later reports concerning the American market from our New York branch.

¹⁾ Berichte d. deutsch. pharm. Ges. 21 (1911), 209.

In a sassafras oil distilled from roots, E. R. Miller and G. H. Marsh¹⁾ have detected the presence of camphor (m. p. of the oxime 115°). This is nothing new, for as far back as the year 1896, Power and Kleber²⁾ observed d-camphor in oil of sassafras-root bark.

A case of poisoning with sassafras oil is mentioned in the *Pharmaceutical Journal*³⁾. A Scotch terrier, which had been treated with the oil for lice, died after a week's treatment, and the post-mortem showed that both the liver and the kidneys were affected. There is no doubt that the cause of poisoning in this case is traceable to the safrol contained in the sassafras oil; this substance, as stated by Kobert in his *Lehrbuch der Intoxikationen*, Vol. II, p. 545, being able to cause serious anatomical changes of a degenerative and fatty character, in particular in the liver, kidneys, and heart.

Savin Oil. The consumption of this oil has so enormously increased in recent years that we have lately experienced difficulty in obtaining sufficient quantities, and as a result of this it has naturally been necessary to raise the price. The collectors of savin-twigs in Tyrol are continually increasing their pretensions owing to the brisk demand for distilling material, and it has been necessary to concede their demands in order to prevent interruption in the supplies. In the end there will be no alternative but to look around for 'other sources of supply, which are hardly likely to fail in view of the wide distribution of the plant.

Spearmint Oil. In accordance with their annual custom, our New York branch have sent a traveller through the growing districts and have ascertained through this representative that in the States of Michigan and Indiana 1727 acres are under spearmint, and that more than one-half of this, *viz.*, 921 acres, represents new plantations. Taking into account the fact that the area under spearmint in 1910 was only 1462 acres, a more abundant yield might have been expected, but the abnormal heat, by injuriously affecting the oil-yield, has disappointed these favourable anticipations. In addition to this, several speculators had secured the output of some of the principal distillers in good time, with the result that before long the prices showed an advance on the previous level, and have lately reached \$ 3.75 per lb. At the present time the market is firm, and there is no prospect of lower prices. In Wayne County, where last year there were still 18 acres under spearmint, our representative was only able to discover 2¹/₂ acres under this crop; and this district may therefore now be struck from the list of producing sections, in all probability for good.

¹⁾ Americ. Perfumer 6 (1911), 85.

²⁾ Pharm. Review 14 (1896) 101; Report April 1896, 68.

³⁾ Pharmaceutical Journ. 86 (1911), 368.

Spike Oil. So far as the present reports go, the result of the crop in the South of France has not been favourable and prices are therefore beginning to tighten.

Dalmatian Spike Oil. Two oils distilled in Dalmatia which were submitted to us for examination some time ago¹⁾ prove that it is possible to prepare suitable spike oil in that country. Both oils had the pleasant, refreshing aroma of the French distillate and gave the following constants:

	d_{150}	α_D	α_D of the initial 10%	acid v.	ester v.
1.	0,9033	$-0^{\circ}53'$	$+0^{\circ}16'$	0,9	5,6
2.	0,9022	$-0^{\circ}10'$	$+2^{\circ}14'$	0,9	5,4

The ready solubility of the samples is worthy of note, both of them giving a clear solution with 4 to 5 vols. 60% alcohol. The slight laevorotation does not denote any abnormality, for we have ourselves at the time obtained in the South of France, from selected material, spike oils which rotated slightly to the left²⁾.

Spanish spike oil. A small parcel of spike flowers has been sent to us from Spain, of which the botanical derivation from *Lavandula Spica*, D. C. (*L. latifolia*, Vill.) was confirmed by a special examination. Distilled with steam, the flowers yielded 1,9% of a brownish-yellow oil showing the following constants: d_{150} 0,9100, α_D $-2^{\circ}20'$, α_D of the initial 10% of the distillate $+1^{\circ}10'$, n_{D20} 1,46823, acid v. 3,7, ester v. 7,0. The oil was soluble in 2 vols. 70% alcohol; when more than 4 vols. of the solvent was used, paraffin separated out and opalescence ensued.

The oil possesses the same characteristics as do the oils which are brought into commerce from Spain under the name of "Spanish lavender oils", so that these oils also are probably in reality spike oils. The darker colour and slightly lower degree of solubility of our sample were due to its more exhaustive distillation.

Staranise Oil. Throughout the summer the quotations for Chinese oil have shown very slight fluctuations from the price of 4/5 cif., but no large transactions have been concluded, because, as compared with the cheap rates ruling at the beginning of last year, this price was by no means an inducement to speculative purchases. It is true that reports of shortage in the arrivals continue to reach us from Hong Kong, but so far as the real position and prospects of the article are concerned, we are depending upon mere suppositions. We lay stress upon this fact because

¹⁾ Comp. foot-note p. 63.

²⁾ Report November 1908, 116.

our customers frequently solicit information from us with regard to the probable course of the market. A few large parcels of Tonquin staranise oil have also been offered, but business was impracticable owing to the stiff-necked attitude of the sellers, who to all appearance are still unwilling to believe that the supplies received from Tonquin during the past few years have not been any better as regards quality than are those Chinese brands which have a reputation for reliability.

In the lowest-boiling fractions derived from a parcel consisting of many tons of staranise oil we have detected the following terpenes: — *d*- α -Pinene¹). A fraction (d_{150} 0,8541; $\alpha_D + 24^\circ 31'$) boiling between 155 and 158° yielded with nitrosyl chloride a nitrosochloride which melted in the crude state between 101 and 103° . The derivative obtained therefrom by reacting upon it with benzylamine had m. p. 123 to 125° .

d- β -Phellandrene¹). This hydrocarbon had accumulated by fractionation in a fraction boiling between 171 and 174° , possessing the following physical constants: d_{150} 0,8489, $\alpha_D + 2^\circ 20'$. The nitrite obtained from it, when recrystallised from acetone, showed the characteristics stated by Wallach for β -phellandrene. It melted at 102° and was lævorotatory in a chloroform solution.

Dipentene and *l*-limonene occurred in the fractions boiling at 178° (d_{150} 0,8510; $\alpha_D - 28^\circ 15'$). The first-named body was identified from the tetrabromide, m. p. 124° . From the acetic ester crystallisation liquors we isolated the most easily soluble portions in the form of crystals melting below 100° , which after being purified once more, gave m. p. 102 to 103° . This substance was obviously limonene tetrabromide. Further proof of the presence of dipentene was afforded by the generation of the nitrosochloride and of the piperidine derivative of the latter (m. p. 153°).

In addition to the above the first runnings under examination contained considerable quantities of fractions boiling between 163 and 168° , with a marked odour of turpentine. The constants of these fractions were as follow: d_{150} 0,8551, $\alpha_D + 14^\circ 7'$, n_{D200} 1,47343. Repeated tests for β -pinene or sabinene by oxidising with permanganate in alkaline solution only gave negative results. We will not omit to add that each of the above-named terpenes only constituted a fraction of perhaps 0,01 % of the total quantity of the original oil.

Th. H. Durrans²) has examined a sample of staranise oil which aroused suspicion on account of its low solidifying point (about $+13^\circ$). In view of the fact that further tests failed to afford positive evidence of adulteration,

¹) We here confirm the statements in our Report of April 1893, p. 62, regarding the occurrence in staranise oil of both these hydrocarbons.

²) *Perfum. and Essent. Oil Record* 2 (1911), 60.

Durrans inclines to the opinion that the sample was either an old oil, or had been partially deanetholised.

In our last Report¹⁾ we discussed the changes which staranise oil undergoes in the process of deanetholisation, especially with the object of demonstrating that the abnormal behaviour of staranise oil is not necessarily always due to adulteration.

The explanations which were given by us on that occasion have induced a Paris business-friend to give us the following information concerning staranise oil, which is not without broader interest: According to our informant the Chinese have at their disposal several qualities of staranise oil; one of these, an inferior quality, comes from the neighbourhood of Pac-Sé, from which originally only the seed was brought into commerce. The solidifying point of this oil is about 11° , whereas the oils from Tonquin and the equally good oils from Ping-Sian have a solidifying point of not less than -16° . By doctoring the last named oils with the first it is possible to prepare mixtures which may be sold with a good profit at low prices²⁾.

Oil of *Strobilanthes lupulinus*. An English periodical³⁾ mentions an oil which is most probably derived from *Strobilanthes lupulinus* (*S. Dalzellii*), an Acanthacea which is very common in the ghauts near Bombay. The oil, which was distilled from the flower-buds, possessed a very strong but decidedly pleasant odour. Its constants were as follow: $d_{40}^{20} 0.9648$, $n_{40}^{20} 1.4688$, $\text{sap. v. } 1.7$, $\text{ester v. } 2.57$. No details are given with regard to the percentage of the yield.

Tansy Oil. The plantations in the States of Michigan and Indiana are smaller in extent this year than in 1910, being only 145 acres against 182 acres last year. At first, owing to absence of demand, the prices had somewhat receded, especially as over 1300 lbs. of old oil had been carried forward into the new season. Lately, however, there has been some recovery, and the article has taken its place in the general upward movement of American oils.

Oil of *Taxodium distichum*, Rich. (Southern Cypress). A. F. Odell⁴⁾, having extracted the sawdust of this North American conifer with 95% alcohol, obtained an extract which, when distilled under diminished pressure (35 mm.) yielded one fraction boiling between 180 and 190° , and another boiling between 217 and 222° . From the first fraction he isolated a body possessing the following properties: b. p. 182 to 185° (35 mm.), $d_{40}^{20} 0.9469$, n_{40}^{20} to the right, $n_{D_{20}}^{20} 1.5040$. Combustion resulted in the formula $C_{12}H_{20}O$;

¹⁾ Report April 1911, 108.

²⁾ On staranise oils of low solidifying point also compare Gildemeister and Hoffmann, *The Volatile Oils*, 1st Ed., p. 352, footnote 4, as well as Report April 1906, 64.

³⁾ *Perfum. and Essent. Oil Record* 2 (1911), 96.

⁴⁾ *Journ. Americ. chem. Soc.* 33 (1911), 755.

the mol. refr. (found 56,29, calc. 53,16) pointed to the presence of two double bonds, a surmise which was confirmed by the absorption of 4 molecules¹⁾ of bromine. The author supposes the new compound to represent an aliphatic aldehyde, to which he has given the name of *cyprial*, and which gives the characteristic aldehyde-reactions with silver nitrate and magenta-sulphurous acid.

The higher-boiling fraction of the alcoholic extract contained a hitherto unknown sesquiterpene, called *cypressene* by Odell, and possessing the following constants: b. p. 218 to 220° (35 mm.), 295 to 300° (778 mm.), d_{40}^{180} 0,9647, $[\alpha]_{D20} + 6,53^\circ$, n_{D220} 1,5240. The mol. refr. was found to be 64,66 (calc. 62,55) which points to the presence of a double bond. In accordance with this supposition the sesquiterpene absorbed 2 molecules¹⁾ of bromine. With concentrated nitric acid of moderate strength cypressene yields a yellow, amorphous oxidation-product; with concentrated sulphuric acid it gives a distinct red coloration.

Oil of Thyme. Roure-Bertrand Fils²⁾ report on an almost colourless thyme oil originating from Syria. The sample contained 43% phenols (thymol and carvacrol) and possessed the following properties: d_{150}^{180} 0,9120, $\alpha_D - 0^\circ 56'$, soluble in 1 vol. and more 80% alcohol.

Turpentine Oil. An instructive review of the entire position of the American turpentine trade and industry, consisting of a symposium of articles written by various contributors whose office or qualifications entitle them to be regarded as authorities, has appeared in a profusely illustrated special number of an American periodical³⁾. It would far transcend the limits of our Report to enter into the particulars of these, in part extremely interesting, articles, and we will therefore content ourselves with quoting the titles and the names of the respective authors, and giving a synopsis of the principal contents of those contributions which contain new information of real importance. The articles conclude with very elaborate statistical tables covering recent years as well as, in part, the distant past, and dealing with the production of oil and rosin, the price-fluctuations of turpentine oil in the course of the last 28 years, the export figures relating to both the above-named products from the year 1880 onwards, the exports to each country of shipment in the past 10 years and the total sales and quotations of the twelve different qualities of resin (WW. to B.).

A. Pridgen: How turpentine and rosins are made in Dixieland. Naval Stores Inspector J. E. Register: The Naval Stores Inspector — His work and how he does it. Supervising Naval Stores Inspector H. M. King:

¹⁾ Probably atoms is meant.

²⁾ Berichte von Roure-Bertrand Fils, April 1911, 24.

³⁾ Savannah Weekly Naval Stores Review and Journal of Trade (Special "Educational" Annual Number) 21 (1911), No. 7, May 27th.

How the purity of Naval Stores is protected. T. Purse, Supt. Savannah Board of Trade: The Savannah Board of Trade, the Naval Stores price-making body of the World. Bd. of Trade President J. A. G. Carson: The relations of the factor to the Naval Stores industry. U. S. Forest Supervisor J. F. Eldridge: How turpentine is worked in Uncle Sam's forests. U. S. Assistant District Forester H. S. Betts: Turpentine experiments out in Arizona. The same: The Longleaf or Turpentine pine of the Southern States. (From Special report.) F. P. Veitch and M. G. Donk, U. S. Dept. Agriculture: Spirits of turpentine, its chemical nature, general properties, production, grading, and uses. (From Special report.) C. S. Saussy: Turpentinizing in the land of the Aztecs. Anonymous: The Naval Stores industry in France. H. A. Grant: Wood turpentine, its failures and its successes.

Pridgen, at the end of his article, contrasts the working costs of a turpentine plantation 15 years ago and the present time, based upon the average crop of 10 500 trees. He concludes that as a result of the rise in wages and in the cost of materials (tools, barrels, &c.) as well as of the increased interest on the minimum capital required (which is now three times as much as formerly), the expenses have almost trebled: the increase being from \$ 851,50 to \$ 2204, nothing being apparently allowed for redemption of capital. Pridgen dwells at length upon several circumstances which embitter the lot of the turpentine producer, such as the so-called Labour laws (originally intended to prevent undue exploitation of the labourers by the employers), which have greatly increased the cost of engaging and transporting coloured labour, and the dangers and privations to which the white operator (as the turpentine-distiller is called), is exposed by having to live with his family in loneliness and far from all civilisation in the virgin forests, surrounded by a horde of, frequently unruly, coloured labourers. The articles by Register, King, Purse, and Carson afford a telling picture of the manner in which turpentine oil and rosin are handled when they have left the place of production and reached the trading centre. All the merchandise as it arrives is most carefully examined by officials known as Naval Stores Inspectors who are experts appointed by the Municipality. These inspectors test the quality, colour and weight of each barrel, &c., and the result of their examination is entered in their records and marked on the packages. A Supervising Inspector, appointed by the State, settles disputes which may result from differences of opinion between the inspector and the producer, or between buyers and sellers. The States of Florida and Georgia were the first to place the trade in turpentine products under control in this manner, and therefore also the first to enact State laws for the protection of the purity of the said products, by which adulteration with other oil, or wilfully untrue or insufficient description, insufficient filling of the barrels, &c. render the offender liable to severe punishment. Purse

mentions that the Board of Trade¹⁾ at Savannah appoints a special committee consisting of two factors and two exporters, the *personnel* of which changes every two months, to which is entrusted the duty of fixing the prices of the twelve brands of colophony and of the different qualities of turpentine oil. I. e. "water white" "standard", "off one shade", "off two shades" and "off three shades" (the last-named. however, is not maketable, — or rather for "turpentine oil" pure and simple, for the various qualities are mixed in order to restrict the sales to one standard quality. The findings of this committee must be those of a majority of the members, and if necessary an additional factor and an additional exporter are elected to sit on the committee.

Mr. Carson, who is himself the head of the senior firm of factors at Savannah, writes on the position of the factor in the industry. The factor is to all intents and purposes the selling agent of the producer, whose home is generally far away in the woods, he is also his confidential man and adviser and not infrequently his banker. He buys up the merchandise and passes it on to the jobbers, who on their part supply the retail tradesmen and other consumers. There are several reasons against the concentration of purchase and sale in one hand (a plan which has already been tried), the principal of these being that the factor keeps no stock, but has to dispose of his goods according to requirements and occasion, as the condition of the market and the prices may demand. In these circumstances it is the dealer or jobber rather than the factor who runs the risk of any fluctuations in price that may occur.

According to Saussy, the turpentine industry in Mexico²⁾ is still in the initial stage; its unfavourable position being mainly due to its scattered character and to the location of the distilleries far from the great railway-lines and main arteries of traffic, and at much higher altitudes. The conditions of labour are said to be good, but Saussy complains bitterly about the constant interference of the tax-collectors, which is unknown in the United States. Not only is there a tax of 10 centavos ($2\frac{1}{2}$ d. or 5 cents) upon every tree which is tapped — an impost which is only remitted under special conditions — but every business-book (cash-book, day-book, &c.) is taxed, every page of every book having to bear a stamp of 5 centavos. These burdens, as well as many others unknown in the United States, such as income-and receipt-taxes, make it difficult for the American citizen to accustom himself to the peculiar conditions of the country.

The present position of the wood-turpentine industry is described by H. E. Grant, Secretary Wood Turpentine Association. It is only within the last few years that wood turpentine has been produced with any degree of success, failures, losses and disappointments having previously been

¹⁾ Perhaps "Chamber of Commerce" better expresses the British idea of the functions of such an organisation.

²⁾ Comp. Report November 1908, 118.

the order of the day. The conditions of sale in particular caused the greatest difficulties, and were only overcome when the Association was established (the plants working by the "destructive process" being excluded) and laid down the standard type of a pure wood turpentine which answers all fair requirements. The Association was also successful in securing the right to substitute for their product the designation "wood spirits turpentine" instead of that of "adulterated spirits turpentine" which is officially prescribed for all oils which are not pure turpentine; a designation which was of course a great stumbling-block in the way of the sale of the wood-spirits. From the consumer's standpoint the principal difference between the two kinds of oil lies in the odour; all other differences are of little importance, except perhaps the somewhat higher temperature (165°) at which the wood turpentine begins to boil, in fact, it might be said that wood turpentine is the purer of the two, because it has been twice distilled; once when it was recovered from the oil by steam-distillation, and again in the subsequent rectification and separation of the heavier oils, whereas genuine turpentine oil has only been distilled once. The young industry has now passed its most difficult time and in view of the declining production-figures of the genuine oil on the one hand and the growing utilisation of the wood-waste of the saw-mills and of the dying, exhausted turpentine-forests on the other, the producer of wood turpentine looks forward to the future with confidence.

The two articles by H. S. Betts deal in a more technical sylvicultural manner with the occurrence and the treatment of the various turpentine-yielding pines of the Southern States, the influence of the old "boxing"-method upon the density of the wood of *Pinus palustris*, the most widely-distributed of the pines (Betts, in contradistinction to other authorities, does not consider that effect to be at all unfavourable), and the application of the wood of the various species to the different purposes of the carpenter, the shipwright, &c. Outside of the true turpentine belt, in the States of Arizona and California, modest beginnings have been made in the collection of turpentine from the Western Yellow Pine. These experiments have given satisfactory results and are to be repeated this year upon a larger scale in those two States and also in that of Colorado.

The articles by Veitch and Donk on turpentine oil, as well as that on the French turpentine industry, do not contain anything that would be new to our readers, and we therefore only quote the titles.

The subjoined figures, which are of general interest, may be culled from the abundant mass of statistical material.

Output of turpentine-oil, in barrels of 50 gallons

	1910	1909	1908	1907	1905
Quantity . . .	555 000	580 000	731 000	684 000	613 000
Value (\$) . . .	17 680 000	12 654 000	14 112 000	18 283 000	15 170 000

Output of rosin, in barrels of 280 lbs.

	1910	1909	1908	1907	1905
Quantity . . .	3 404 000	3 258 000	4 288 000	4 000 000	3 508 000
Value (\$) . . .	18 255 000	12 577 000	17 783 000	17 317 000	8 726 000

Exports of turpentine-oil, in gallons

	1910	1909	1908	1907	1906	1905
Quantity	14 252 321	16 061 783	19 433 181	17 176 843	16 182 500	15 894 813
Value (\$)	9 627 428	7 779 728	8 301 747	10 214 610	10 320 926	8 902 101

Exports of rosin, in barrels

	1910	1909	1908	1907	1906	1905
Quantity	2 269 339	1 984 525	2 601 181	2 636 149	2 481 269	2 310 275
Value (\$)	12 373 825	8 211 650	9 661 029	11 932 701	10 416 320	7 069 084

The statistical data dealing with the wood-distilling plants situated in the turpentine belt do not show whether only plants where wood is distilled by steam or also those which work by the destructive process have been included. But however that may be, these figures, which have at any rate been compiled on a uniform principle, are of interest insofar as they show the fluctuating development of this young industry in each of the three years under review: —

	1909	1908	1907
Number of plants	31	30	31
Cords ¹⁾ of longleaf pine wood			
worked up	99 686	90 991	61 149
Value of same (\$)	241 726	207 202	210 844
Value of all other materials (saw-			
mill waste, &c.) (\$)	15 624	8 221	1 200
Total value of all products (\$) . .	686 794	491 161	534 802
Turpentine Oil, gallons	682 280	505 800	654 711
" " value (\$)	243 491	166 343	304 860
Charcoal, bushels	2 403 401	1 995 728	1 158 364
" " value (\$)	210 007	186 616	102 411
Oil, gallons	322 226	304 979	391 916
" " value (\$)	70 080	56 043	69 399
Tar, gallons	1 364 984	966 675	760 836
" " value (\$)	104 671	81 349	58 132
Pyroligneous acid, gallons	4 850	8 100	—
" " value (\$)	218	810	—
Value of all other products (\$) . .	58 317	—	—

¹⁾ 1 cord = 8 × 4 × 4 feet.

According to British Consular Reports¹⁾ the exports of turpentine products (oil and resin) from Bordeaux and Bayonne, the two principal shipping-ports in the French turpentine district, during the past two years have been as below: —

<i>Bordeaux</i>		1909	1910
Turpentine products	46739 tons (Engl.)	46571 tons (Engl.)	
of which was shipped to U.K.	16557 " "	15595 " "	
including turpentine oil	3674 " "	4972 " "	
of which was shipped to U.K.	1256 " "	1359 " "	
<i>Bayonne</i>			
Turpentine products	20823 tons (metr.)	20503 tons (metr.)	
of which was shipped to U.K.	— " "	1989 " "	

The Imperial Institute²⁾ in London has examined two samples of Indian turpentine oil from *Pinus longifolia* (Chir-Pine). The samples gave the following constants: d_{15}^{150} 0,871, α — $0^{\circ} 45'$ and d_{15}^{150} 0,868, α — $2^{\circ} 10'$. When fractionated, scarcely any of the oil passed over below 165° . A similar behaviour was exhibited by an oil previously examined at the Imperial Institute. The last-named sample consisted to the extent of one-third of l-pinene, and also contained sylvestrene, mixed with other high-boiling terpenes. As stated by us in our last Report, an oil from *Pinus longifolia* which was examined by us³⁾ was also found to contain a considerable proportion of sylvestrene, as well as a sesquiterpene.

A method for the estimation of turpentine oil worked out by P. Klason⁴⁾ is based upon the conversion of the pinene peroxide which is present in this oil with cymene mercaptane, cymene disulphide being formed. As cymene mercaptane can be titrated with decinormal iodine solution (according to the equation $2RSH + 2I = R_2S_2 + 2HI$) it is possible to control the quantity of mercaptane which is used up. For the purposes of this estimation a solution of 5 cc. cymene mercaptane in 100 cc. alcohol is required; this solution is standardised with decinormal iodine solution. Next, 5 cc. of the oil under examination and 5 cc. mercaptane solution are poured into a flask of about 30 cc. capacity. After filling up with alcohol the flask is vigorously shaken and left to stand for 24 hours. As a rule the reaction is completed at the end of this period. The contents of the flask are now diluted with about 100 cc. alcohol and titrated with decinormal iodine solution until a brown colour appears. No starch-solution should be used as an indicator.

¹⁾ Diplomatic and Consular Reports May 1911, Nr. 4659, p. 14, 26, 40.

²⁾ Bull. Imp. Inst. 9 (1911), 8.

³⁾ Report April 1911, 116.

⁴⁾ Chem. Ztg. 35 (1911), 537.

When freshly-distilled turpentine oil is left exposed to the air in a beaker, the peroxide-content gradually increases until at last a maximum is reached. French turpentine oil has shown the highest peroxide-formation; the values for dipentene and terpinolene are considerably less, while the power of activity of sylvestrene is much lower than that of pinene.

Some years ago, Frey¹⁾ published a method of testing turpentine oil for petroleum by shaking with three times its volume of aniline. The practical usefulness of this test, which in our reference we had only admitted under reserve, has recently been commented upon by H.S.Shrewsbury²⁾, who only admits it so far as concerns additions of petroleum of not less than 30 or more than 70%, this limitation having been confirmed by special experiments with mixtures of known petroleum-content. Moreover, the accurate values which came within these limits can only be arrived at by errors compensating each other.

An article by George Walker³⁾ on methods for the utilisation of wood-waste deals in the first place with the exploitation of such waste in the United States by means of fire-distillation for the purpose of gas- and tar-manufacture, and next with the utilisation of soft-wood waste by steam-distillation. We have repeatedly referred⁴⁾ to the properties of the purified distillate obtained by the last-named method, the so-called wood turpentine oil. Walker gives a short description of a plant installed by him for treating "light-wood", *i. e.*, the heart-wood of dead turpentine-trees in which, when the bark and the sap-wood have decayed, nearly the whole of the resin concentrates. This wood is treated in cylindrical retorts holding about 1 cord (about 128 cubic feet) each, and is first subjected to simultaneous distillation with live steam and with fire, the product of this operation being "turpentine oil". Afterwards it is again distilled with fire only, when it yields "heavy oil". At the end of the distilling, when the retort is opened, steam is again injected, with the object of blowing the oily matter out of the condenser and of quenching the glowing charcoal. The heavy oil is again subjected to distillation, when it first yields a resinous oil, sp. gr. about 0,88, and subsequently a heavier oil containing about 20% creosote and a large proportion of paraffin. A residue of about 25% is left, consisting of an elastic glossy black pitch. Walker also describes a method which he has worked out for isolating the resin from finely divided light-wood from which the oil has been removed by steam-distillation, by extracting it with volatile solvents. In a plant working by this method 200 barrels of resin are made weekly, and as this process

¹⁾ Comp. Report November 1908, 123.

²⁾ Analyst 36 (1911), 137. Quoted from Chem. Zentralbl. 1911, I. 1560.

³⁾ Journ. Soc. chem. Industry 30 (1911), 934.

⁴⁾ Comp. Report April 1907, 98; October 1907, 94, 95; October 1909, 122, 124; this Report p. 90.

is said to yield as much resin in twelve hours as could be obtained by the old "boxing"-method in about twenty years (!?), Walker believes that in the course of time his method will supplant the present processes in vogue in the turpentine-industry, seeing that, in the opinion of experts, the supplies of light-wood, notwithstanding it is largely used for railway-sleepers, are large enough to cover the world's requirements of turpentine-oil and resin. A further possible source of employment of the oil which has been freed from oil and resin is to be found in the wood-pulp industry, and Walker unfolds a picture of the future in which the lumber-, turpentine- and wood-pulp industries will be placed upon a common silvicultural basis.

Vetiver Oil. So far as regards oil of our own distillation, which is unquestionably preferred by the perfumers, prices have remained unaltered, seeing that sufficient quantities of excellent vetiver root were available from Java and that we had therefore no difficulty in replenishing our stocks. On the other hand it has been found necessary, in the course of the summer, to advance the quotations of the cheaper oil from Réunion, because all the parcels which could be discovered in the European markets proved to be seriously adulterated. Reports are current that the production has lately been much reduced owing to its unremunerative character, yet the fact remains that from the beginning of January to the end of July 1911 about 446 kilos were exported, as compared with 506 kilos in the corresponding period of 1910. No very large decrease in the production is therefore evident at present.

Wallflower Oil. From the flowers of wallflower (*Cheiranthus Cheiri*, L.; N. O. Cruciferae) E. Kummert¹⁾ obtained by means of extraction with solvents of low b. p. a dark-coloured extract of an ointment-like consistency. The extract was freed from wax and vegetable fats by means of strong alcohol and subsequently subjected to steam-distillation. By this method the author obtained a yield of 0,06% of an oil possessing the following constants: b. p. 40 to 150° (3 mm.), d_{15}^{20} 1,001, acid v. 0,35, ester v. 20,0, sap. v. 20,35. In the concentrated state the oil had a disagreeable odour, when strongly diluted it reproduced the natural odour of the flowers.

Distilled *in vacuo* at 3 mm. only small proportions of bodies boiling below 40° passed over. These bodies had an unpleasant odour, and were probably compounds of the nature of mustard oil²⁾. The higher-boiling fractions, when treated with semicarbazide, yielded a small proportion of a semicarbazone-mixture which was decomposed with oxalic acid, when an odour of hawthorn and violets became perceptible, a fact which may point to the presence of anisic aldehyde and irone.

¹⁾ Chem. Ztg. 35 (1911), 667.

²⁾ Wallflower seed contains a sulphone, cheirolin, in a glucoside-like combination. Comp. Report October 1910, 85.

When the oil, after being freed from ketones and aldehydes, was treated with phthalic acid anhydride, nerol (m. p. of the diphenylurethane 50°), geraniol (m. p. of the diphenylurethane 82°) and benzyl alcohol (m. p. of the phthalic ester 106°) were found present. The oil further contains linalool (m. p. of the phenylurethane 65°). In the saponification liquor Kummert, after removing traces of phenols (perhaps p-cresol) and lactones (perhaps coumarin-like compounds) found acetic acid, salicylic acid (m. p. 156°) and anthranilic acid (m. p. 145°).

The fractions with the highest b. p. had a well-marked odour of indole; they were mixed with three times their volume of ether and precipitated with sulphuric acid. From the precipitate, decomposed by hot soda-solution, Kummert isolated the methylester of anthranilic acid. The bases, when freed from ester, were diluted in light petroleum with picric acid, giving rise to a red picrate from which, upon decomposition with soda solution, indole (m. p. 52°) and a small proportion of bases with an odour reminding of pyridine were obtained.

Wax Oil. Wax oil is an obsolete pharmaceutical preparation, obtained by subjecting beeswax to dry distillation with from twice to six times its weight of lime or, (but only rarely) without any addition whatever. Occasionally it is still employed as a remedy for external use. Th. Ekecrantz and E. Lundström¹⁾ have recently investigated the oil. They took pure beeswax and subjected it to distillation three times with twice its weight of lime, when they obtained about 67,5% of a brownish-yellow oil, which at ordinary temperature gradually solidified into a greyish yellow mass, studded with crystalline leaflets. The saponified product, when distilled by steam, yielded an oil of sp. gr. 0,7825 (15°), consisting of a mixture of saturated hydrocarbons. The major part of the wax oil was not volatilisable with steam and consisted of noneikosane, C₂₉H₆₀. Noneikosane is not an original constituent of the wax but is the product of the myricylic alcohol which is present in the wax in combination with palmitinic acid.

Wintergreen Oil, Indian. Mr. Werner Reinhart, of the firm of Gebr. Volkart, of Wintherthur, to whom we are already indebted for many interesting communications on the production of essential oils in India, has now added to our obligations by sending us a short account of the preparation of Indian wintergreen oil, and it is our pleasant duty here to express our thanks to Mr. Reinhart for this kindness. The parent-plant of this little-known oil²⁾ is *Gaultheria fragrantissima*, Wall. (*G. fragrans*, D. Don.; *G. punctata*, Blume; *Arbutus laurifolia*, Buch.-Ham., N. O. Ericaceæ). This plant occurs gregariously over extensive tracts of the higher Nilgiri-region, and is also frequently met with in the Palni and Travan-

¹⁾ Arch. der Pharm. 248 (1910), 500.

²⁾ Gildemeister and Hoffmann, *The Volatile Oils*, 1st Ed., p. 589.

core Hills, South of that district. It differs markedly in its habit from *G. procumbens*, L., the parent-plant of the American wintergreen oil, which is a small, creeping shrub, while *G. fragrantissima* grows into a strong, high bush.

The oil is prepared by the natives in the neighbourhood of Ootacamund (Nilgiris) by simple distillation of the leaves with water in primitive copper stills, such as are employed in India in the manufacture of grass-oils, among others. The output is quite insignificant, the producers being mostly distillers of eucalyptus oil who make a little wintergreen oil in addition. It would, however, be quite possible to extend the industry, seeing that there is abundance of raw material available.

The oil-yield is very small, and the distilling is therefore actually not profitable. The sale of the oil is wholly restricted to home-consumption, and the demand for the article appears to be only slight. The high market-price of the oil locally (about 40 *Rs* per kilo), as well as the competition of the American article and of the synthetic product stand in the way of establishing an export-trade to Europe.

Mention is made of Nilgiri wintergreen oil in Government Reports as far back as the 'forties of the 19th century.

A sample of the oil which accompanied Mr. Reinhart's communication to us, and which had been obtained by him on the occasion of a visit to a distillery in the Nilgiris, entirely resembled the oil from *Gaultheria procumbens*, both in its odour and in its other properties; but it was inactive, whereas the latter is faintly laevorotatory: $d_{20} = 1.1877$, $n_D = 1.53485$, ester v. 364.8 — 99° methyl salicylate, sol. in 7 vols. a. m. 70° alcohol. The oil had a reddish-brown colour.

From a paragraph in the Bulletin of the Colonial Museum at Haarlem¹⁾ it appears that *Gaultheria fragrantissima* also occurs in the high mountains of the Dutch Indies, in Java as well as in Sumatra. Its Malay name is "*Sari moedjari*". The oil obtained from this species and from the allied *Gaultheria leucocarpa* is known in the producing district as "Goendapoeri oil", and is employed medicinally and as a perfume; it is used, among other purposes, as a scent for the garments of Indian Princes. In Sumatra the leaves are chewed as a species of "*Sirih*"²⁾.

Wormseed Oil. As in the past, the American variety has been in brisk demand, its reputation as an anthelmintic being steadily on the increase. It is true that the increase in price which we prognosticated in April has actually taken place since then, but the sale has not been affected thereby in the slightest degree. Unfortunately no reports are as yet to hand concerning the coming crop. Levantine wormseed oil is still

¹⁾ Bulletin No. 48 van het Koloniaal Museum te Haarlem, July 1911, p. 125.

²⁾ "*Sirih*" is a masticatory much esteemed among the Malays. Various aromatic herbs are used in its preparation.

wanting, owing to the impossibility of conceding the prices which are demanded for the raw material. Apparently the consumers are not at all troubled by the total absence of this particular variety.

A paper by E. K. Nelson¹⁾ on chenopodium oil makes a valuable contribution to our knowledge of the chemical characteristics of the body $C_{10}H_{16}O_2$ which was isolated by us from this oil some years ago²⁾, and to which we gave the name of ascaridol. The author examined four samples, which he had procured in Maryland, the producing country. The constants of these samples were as follow: d_{25° 0,955 to 0,9691, α_D — 5,4 to 8,8°, n_{D25° 1,4723 to 1,4726, sol. in from 3 to 7 vols. 70% alcohol. A fifth sample, at least one year old, which was used for the purposes of the examination recorded below, gave: d_{25° 0,9694, α_D — 0,35°, n_{D20° 1,4780, sol. in 3 vols. 70% alcohol, acid v. 0, ester v. 5,0. In addition to ascaridol: b. p. 96 to 97° (8 mm.), d_{20° 0,9985, α_D + 0,7°, n_{D20° 1,4719, Nelson isolated cymene and *d*-camphor, both of which bodies had already been detected by us at the time as constituents of the oil. The results obtained by shaking ascaridol with saturated solution of ferrous sulphate are, however, of particular interest. At ordinary temperature this peculiar reaction proceeds with such violence as to decompose the ascaridol, the temperature rising considerably with evolution of a combustible gas³⁾. Isopropyl alcohol is also formed as a product of reaction and was isolated from the syrupy product of conversion by steam-distillation and identified as acetone by oxidising it with chromic acid (dibenzylidene acetone, m. p. 111 to 112°). Below 35° the reaction proceeds normally and without decomposition. In these conditions ascaridol adds the elements of the water and is converted into a glycol, $C_{10}H_{18}O_3$ which, when benzoated by Schotten-Baumann's method, yields a solid benzoate, m. p. 136 to 137°. Saponification of this ester yields the pure glycol, in the form of a colourless and odourless, syrupy oil, b. p. 271 to 272°, from which, after prolonged standing in a vacuum desiccator solid crystals, m. p. 62,5 to 64° are precipitated. The glycol $C_{10}H_{18}O_3$ gave the following constants: d_{20° 1,0981, α_D + 0, n_{D20° 1,4796, mol. refr. 48,63 (calc. 48,65). The fact that the body $C_{10}H_{18}O_3$ possesses a second OH-group is shown by the formation of a dibenzoate, which occurs when the glycol is heated for 2 hours with benzoic anhydride to 150°. From alcohol, the ester crystallises in needles, m. p. 116,5 to 117,5°.

In all probability the third oxygen-atom is contained in the molecule $C_{10}H_{18}O_3$ in the form of oxidic oxygen. When the glycol is melted with caustic potash or boiled with sodium, it is converted in part into a compound

¹⁾ Journ. Americ. chem. Soc. 33 (1911), 1405.

²⁾ Report April 1908, 109.

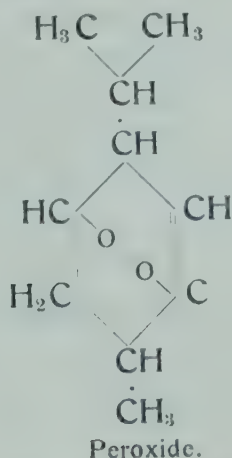
³⁾ The occurrence of a combustible gas as a decomposition-product of ascaridol was first noticed by us at the time.

which acquires a greenish-violet colour when exposed to air. When acidulated and diluted with ferric chloride there passes over with steam a body which, when dissolved in ether, absorbs caustic potash solution with violet coloration. Upon acidulation this body yielded a small proportion of orange-coloured crystals, m. p. 164 to 166°, evidently α -hydroxythymoquinone. These crystals gave a reddish-purple colour with concentrated sulphuric acid. Their aniline-derivative crystallised in deep violet needles.

When the glycol is oxidised with neutral permanganate solution it yields, in addition to a mixture of volatile acids (acetic acid, butyric acid?), a dibasic acid $C_{10}H_{16}O_5$, very sparingly soluble in water, m. p. 116,5 to 117°. This is ascaridic acid, the silver salt of which is almost insoluble in water. Its behaviour towards acetic anhydride, hydroxylamine, or semicarbazide shows that the molecule of the acid contains neither a hydroxyl- nor a ketone-group, while its behaviour when titrated makes it clear that it cannot be either an anhydride or a lactone. When heated above its melting-point, methylheptenone¹⁾ is apparently formed. When oxidised the glycol yields yet another solid dibasic acid, melting at 186 to 187°, to which Nelson assigns for the present the structural formula $C_{10}H_{16}O_6$.

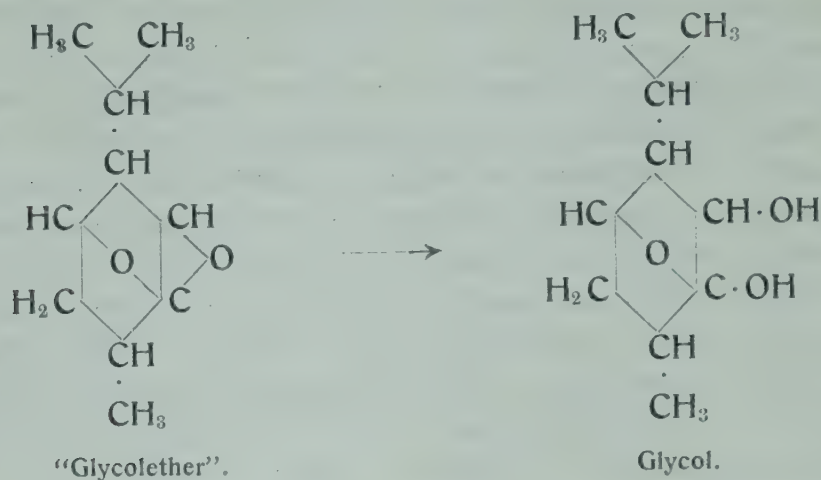
The product of conversion of ascaridol, which was prepared by us at the time by heating a mixture of equal parts of ascaridol and cymene, when shaken with 2% sulphuric acid under cooling, also yields the above glycol, m. p. 62,5 to 64°, which when treated further by Schotten-Baumann's method, yields a monobenzoate, m. p. 136 to 137°. This reaction proves at the same time that in the reaction of ferrous sulphate with ascaridol the absorption of the elements of water is attended by a rearrangement of the molecule. The fact that ascaridol, therefore, cannot be regarded as a true anhydride of the glycol $C_{10}H_{18}O_3$ is further attested by its not absorbing water when exposed to the action of 2% sulphuric acid or of solutions of ferric oxide salts.

From the above data the author concludes ascaridol to be a peroxide possessing the following constitution:



¹⁾ While distilling the acid $C_{10}H_{16}O_4$, obtained by us in the course of permanganate oxidation, we determined beyond doubt the formation of methylheptenone.

Also that, when acted upon with ferrous sulphate, it forms the reaction-products set forth in the subjoined structural formulæ:



According to W. Salant¹⁾, when American wormseed oil is given to cats it acts first as a temporary excitant, and afterwards produces general paralysis and coma. A dose of 0,2 cc. per kilo weight of the animal, administered by the stomach, caused death within 24 to 48 hours. The active constituent of the oil, ascaridol, acts nearly twice as powerfully as does the oil itself, and reduces the blood-pressure.

Wormwood Oil. Of the two varieties of this oil which remained after the disappearance of the French article, that distilled by ourselves from plants grown in our fields at Miltitz undoubtedly enjoyed the greater demand, in particular because we were able, notwithstanding the unfavourable climatic conditions, to continue to offer at the previous price. Our wormwood-plantations have tolerably well withstood the tropical heat and the drought, and this year also have yielded two, albeit by no means abundant, cuts. Therefore, unless an unforeseen demand should set in, or perhaps some surprise should be in store on the part of the United States, we intend to leave our quotations unchanged. In the United States, however, the market has lately become much firmer, because almost the entire output is said to have already passed into firm hands, and speculators are doing their utmost to drive the prices upwards. The representative employed by our New York branch has ascertained the area under wormwood in Michigan and Indiana to amount to 404 acres (as compared with 395 acres last year) and the probable output to about 8000 lbs. In Wayne Co., New York, 21 acres are cultivated with wormwood, their yield being estimated at 370 lbs. As the world's consumption will need to be satisfied with the above-named quantities, the price-prospects for American

¹⁾ Journ. of Pharmacology and experimental Therapeutics 2 (1911), 391. Quoted from Therap. Monatsh. 25 (1911), 498.

wormwood oil may well be regarded as very favourable, provided the parties who control the crop know how to handle the market to their own pecuniary advantage.

An oil prepared in Dalmatia from wild-grown wormwood¹⁾ gave sp. gr. 0,9188 (15°); acid v. 1,3, ester v. 64,4. It was soluble in its own vol. 80% alcohol, the solution remaining clear when more alcohol was added. So far as aroma is concerned, this oil, which has a brown colour, is by no means able to compete with wormwood oil from cultivated herb. It is possible that the parent-plant of this oil was not *Artemisia Absinthium*, L., but another species of *Artemisia*, but we have been unable to obtain any information with regard to this.

As a result of the Acts prohibiting the use of absinthe²⁾ which have been passed in France and Switzerland, a whole series of papers dealing with methods of estimating thujone in liqueurs have made their appearance in recent years, and have been referred to more or less in detail in these Reports³⁾. The decree regulating the enforcement of the Swiss Federal Act on the Prohibition of Absinthe of 5th October 1910, prescribes *inter alia* that the quantitative estimation of thujone shall be carried out by Legal-Cuniasse's method, as modified by Rocques. This decree has led H. Enz⁴⁾ to call attention to the disadvantages of the said method and to propose certain improvements on it. But, according to Enz, the determination of thujone will still remain uncertain, because certain other constituents of the oil, when treated with the reagents mentioned in the method, also give a red coloration which resembles that of the thujone reaction, hence a positive result of the test does not warrant the absolutely certain conclusion that thujone is present, although the non-occurrence of the red coloration is proof of the absence of that compound. We must content ourselves with this brief reference to Enz's paper, and we may mention at the same time that E. Philippe and Th. v. Fellenberg⁵⁾ have also published a short article criticising several of Enz's statements, in answer to which the latter has published a rejoinder⁶⁾.

R. C. Roark⁷⁾ reports on an unusual oil of wormwood oil which was distilled about 10 years ago by A. S. Drew, of Farris Corners, Wis., U. S. A.

¹⁾ Comp. foot-note p. 63.

²⁾ Report April 1907, 103; April 1908, 119; November 1908, 128; April 1909, 92.

³⁾ Report April 1907, 103; October 1907, 98; November 1908, 127; April 1909, 92; October 1909, 129.

⁴⁾ Schweiz. Wochenschr. f. Chem. u. Pharm. 49 (1911), 337.

⁵⁾ *Ibidem* 418.

⁶⁾ *Ibidem* 507.

⁷⁾ Midland Drugg. and pharm. Review 55 (1911), 237.

The oil had a minty odour and was of a very dark colour; its constants being as follow: d_{20}^0 0,9168, sap. v. 150 to 151 (after 40 minutes), 182 to 183 (after 90 minutes). The oil was acetylated and then gave sap. v. 234,8 to 236,2.

The author found the saponification-liquor of the original oil to contain formic and salicylic acids, which he identified from the silver-salts.

The non-saponified oil boiled principally at about 196° and consisted chiefly of thujone.

Oil of *Xanthoxylum ochroxylum*. According to a communication by M. Leprince¹⁾, the bark of *Xanthoxylum ochroxylum*, D. C. (N. O. Rutaceæ) known in Venezuela as "Bosuga blanca", when treated with light petroleum, yields 6% of an oil possessing a sp. gr. of 0,945 (15°). The oil has a stinging, acrid, astringent taste and a refreshing odour. It cannot be distilled at ordinary temperature and is only saponifiable to a slight extent. The substance is probably a mixture of fatty and essential oil.

Ylang-Ylang Oil. The supplies of our popular "Sartorius" brand, which holds unquestionably the premier place among the numerous Manila-qualities, have continued to be regular during the past few months, and as the demand likewise left nothing to be desired, no heavy stocks have accumulated at our works. The competition on the part of the cheap Réunion ylang-ylang oils has been but little noticeable, which shows the difference in quality between the two varieties to be so very wide that the considerable difference in price is of no account in this matter. Up to the end of June the shipments of ylang-ylang oil from Réunion amounted to 1510,5 kilos, which is about equal to the shipments in the corresponding period of 1910 (1560,4 kilos). Lately there has been some fresh talk of ylang-ylang oil distillation in Madagascar and the adjacent islands²⁾, but it would appear that up to the present no one has taken this new industry in hand in a workmanlike way in those islands.

From the Biological-Agricultural Institute at Amani (German East Africa) we have received four samples of ylang-ylang oil³⁾ which had been prepared on a small scale in the laboratory there. The raw material was the same in all cases, except as regards its condition, one oil having been prepared from fresh flowers, and the other three after the flowers had been kept respectively 24 hours, two days, and four days. The results of our examination are given in the table below:

¹⁾ Bull. Sciences pharmacol. 18 (1911), 345.

²⁾ Report October 1909, 129.

³⁾ On experiments in the cultivation of the ylang-ylang tree at Amani comp. Report April 1909, 94.

	1.	2.	3.	4.
Condition of the material	Fresh flowers	Faded flowers after 24 hours' keeping	Faded flowers kept for 2 days and partly somewhat shrivelled	Faded flowers kept for 4 days and dried in the shade
$d_{15^{\circ}}$	0,9366	0,9190	0,9170	0,9382
α_D	$-17^{\circ} 1'$	$-20^{\circ} 4'$	$-19^{\circ} 50'$	$-18^{\circ} 46'$
$n_{D20^{\circ}}$	1,48451	1,48431	1,48267	1,49394
acid v.	1,1	1,1	1,9	2,8
ester v.	136,3	103,8	96,9	114,2
Solubility	in 8 vols. a. m. 70% alc. with opalescence	in 1 vol. 80% alc., dilute sol. opal.	in 1 vol. 80% alc., dilute sol. turbid	in any prop. 90% alc., dilute sol. opal.

Apart from the strikingly low rotation, which would correspond with that of cananga oil, the general constants of the four samples agree with those which have thus far been observed in ylang-ylang oil, but some of the samples in question are very much more soluble, which shows that they contain very little sesquiterpene. That would be an advantage rather than otherwise, but notwithstanding this, samples 2, 3 and 4 were quite useless for perfumery purposes because their aroma was wholly insufficient, and steadily deteriorated according to the age of the raw material used. Only the oil prepared from the fresh flowers could at best be described as usable, but the aroma of this oil, too, was more akin to that of ordinary cananga oil. We regard it as doubtful whether it would be possible, by suitable further treatment (fractional distillation), to prepare from the sample an ylang-ylang oil which would be able to meet competition. We are also doubtful whether a better result would be obtained by fractional collection of the distillate. In our view the manufacture of ylang-ylang oil in German East Africa is not to be recommended for the present, the more so because just now the article suffers already from over-production¹⁾).

In an article on the odoriferous plants of the French Colonies which has appeared in the last Report of Roure-Bertrand Fils²⁾), reference is made to the cultivation of the ylang-ylang tree on the island of Réunion.

¹⁾ Comp. Report April 1909, 93; October 1909, 129; April 1910, 122; October 1910, 144; April 1911, 121.

²⁾ Berichte von Roure-Bertrand Fils, April 1911, 36.

As we have already repeatedly and in detail reported on this subject, we will content ourselves with quoting a few particulars from the interesting article in completion of our previous references¹⁾.

The ylang-ylang tree is not indigenous in Réunion, but it cannot be said with certainty when it was introduced there. It was possibly brought to the island about the year 1770, concurrently with the seed of spice-trees which had been collected by the French captain d'Etchevery in Ceram and the neighbouring islands of the Dutch East-Indies.

A few years ago, in 1906 and 1907, there raged in Réunion a veritable ylang-ylang craze: everybody wanted to possess his own ylang-ylang plantation. The seed was sold at fairly high prices, but much of it was poor or even useless into the bargain. For instance, seed was offered for sale which had been scalded in hot water, as well as unripe fruit to which an appearance of maturity had been artificially imparted.

The example of Réunion soon spread to Madagascar, Nossi-Bé, Mayotta, and the Comoro Islands, but planters in these islands had some difficulty in procuring the necessary material for their cultures, because the people of Réunion were afraid of competition and tried to prevent the exportation of the seed.

The quantity of oil exported in the year 1909 amounted to nearly 1400 kilos.

New Essential Oils. .

Oil of *Artemisia cœrulescens*, L. Of this plant, which belongs to the N. O. Compositæ, and occurs on the littoral of the Mediterranean and, in parts, on that of the Atlantic, a sample has reached us from Turin under the name of *Erba Santa Maria*. We obtained from it 0,24% of an oil which, in its odour, showed a certain similarity to oil of hyssop, but at the same time reminded somewhat of ambrette. At room temperature it appeared as a brownish, butter-like mass, studded with white crystals, which only between 35 and 40° dissolved into a pale brown liquid. Its constants were determined as follows: d_{400} 0,9179, α_D - 5° 50', acid v. 11,3, ester v. 42,0, insoluble in 80% alcohol, soluble in any proportion in 90% alcohol, with separation of a solid substance. The crystals isolated from the oil, after being recrystallised from alcohol, formed fine, white odourless needles, m. p. 108°; so far their chemical characteristics have not been further investigated.

¹⁾ Report April 1902, 68; April 1904, 89; November 1908, 128; October 1909, 130; April 1910, 122.

Cardamom Root Oil. From cardamom-roots from Indo-China we have obtained a yield of 0,64% of a lemon-yellow oil possessing a peculiar, aromatic odour, which bears no resemblance to that of the oil from seed. So far our attempts to ascertain the parent-plant of the oil have been unsuccessful. The oil gave the following constants: $d_{15} 0,9066$, $\alpha_D - 32^\circ 57'$, $n_{D20} 1,48151$, acid v. 3,7, ester v. 87,9, ester v. after acetylation 96,7. The oil was soluble in 0,5 vols. 95% alcohol; when more alcohol was added the mixture rapidly turned turbid, and did not become clear again until the solvent had been increased to 4 vols. Fractional distillation under diminished pressure (5 mm.) gave the following result:

1.	to	35°	5,4%	$\alpha_D - 0^\circ 10'$
2.	35	„ 40°	8,7%	$\alpha_D - 0^\circ 32'$
3.	40	„ 100°	5,4%	$\alpha_D - 17^\circ 5'$
4.	100	„ 110°	10,6%	$\alpha_D - 31^\circ 10'$
5.	110	„ 115°	44,2%	$\alpha_D - 45^\circ$
6.	115	„ 145°	6,4%	$\alpha_D - 33^\circ 14'$
7.	residue		19,3%	$\alpha_D - 39^\circ 15'$

Fractions 1 and 2 contained cineol, which was identified from the double-compound it gave with resorcinol. From fractions 4 and 5, a portion boiling between 117 and 120° (5 mm.) was separated by repeated fractionation. Saturated with hydrochloric acid gas in dry ethereal solution at -18° , this fraction yielded a hydrogen chloride compound which, when recrystallised from methyl alcohol had m. p. 79 to 80°. The hydrochloride was inactive; the chlorine-determination gave the following result:

0,4306 subst.: 0,5928 g. AgCl		
	Found	Calc. for $C_{15}H_{24}, 3HCl$.
Cl	34,06%	33,9%

Our surmise that we had here before us the hydrochloride of bisabolene was confirmed by further examination. With sodium acetate and glacial acetic acid a sesquiterpene was eliminated from it which, when twice fractionated, was found to possess the following constants: 265 to 267° (757 mm.), $d_{15} 0,8748$, $\alpha_D + 0^\circ$, $n_{D20} 1,49063$. With hydrochloric acid this hydrocarbon yielded again the trihydrochloride melting between 79 and 80°.

The residue of distillation of cardamom-root oil solidified at about 15° with separation of paraffin; the last-named body, when recrystallised from alcohol, melted at 62 to 63°.

This examination shows the presence in cardamom-root oil of cineol, bisabolene and a paraffin; bisabolene being the principal constituent.

Cedarwood Oil, East African. The wood of the red cedar (*Juniperus virginiana*, L.) which comes from Florida and is used in the manufacture of lead-pencils, is becoming more and more scarce, but up to the

present no other wood has been found capable of replacing it, which is all the more regrettable because in all probability there does not exist another industry so wholly dependent upon a single kind of wood. Recently, however, large forests of a cedar-species which affords a wood apparently very suitable for pencil-making, have been discovered in German East Africa¹⁾.

A short time ago we were enabled to distil a large parcel of the wood of this East African cedar. Dr. Giessler informed us that the wood was derived from *Juniperus procera*, Hochst., a tree which occurs in the mountains of Abyssinia and Usambara, as well as on the slopes of the Kilimanjaro and the Kenia. The tree grows at altitudes of from 4500 to 9000 feet and in Usambara it forms extensive forests. In its anatomical structure the wood bears a great resemblance to that of *Juniperus virginiana*.

Shavings and short planks constituted our raw material. The former yielded by distillation 3,2% of a deep-yellow, liquid oil with an odour distinctly resembling that of vetiver, and giving the following constants: $d_{15^{\circ}}$ 0,9876, $n_{D20^{\circ}}$ 1,50893, acid v. 14,9, ester v. 8,4, ester v. after acetyl. 70. The oil itself being too dark to permit the reading of its opt. rot., this constant was determined from a solution of equal volumes of oil and alcohol, and found to be $-3^{\circ}43'$, in a 2 cm.-tube, which would correspond with a rotation of $-37^{\circ}10'$ in a 100 mm.-tube for the original oil. The oil was soluble in 1,6 vols. a. m. 80% alcohol and in one half its own vol. a. m. of 90% alcohol.

The short planks, after being broken up, yielded about 3,2% of an oil which formed at ordinary temperature a semi-solid mass studded with crystals. When drained off from the crystals the oil gave the following constants: $d_{15^{\circ}}$ 1,0289, $n_{D20^{\circ}}$ 1,51011, acid v. 27,06, ester v. 7,93, ester v. after acetyl. 89,6. In this case also it was impossible to ascertain the rotation of the original oil; but when diluted with its own volume of alcohol, it gave $-3^{\circ}15'$ in a 20 mm.-tube, equal to $-32^{\circ}30'$ in a 100 mm. tube for the original oil. The oil was soluble in 2 vols. a. m. 80% and in one-half its own vol. 90% alcohol. The crystals consisted of cedar camphor. Recrystallised from alcohol they melted at 86 to 87°, sp. rot. $+10,12^{\circ}$ (2,5517 g. substance dissolved in 25 cc. chloroform). The phenylurethane melted at 106,5°.

Oil of Cinnamomum Burmanni. Two lots of cinnamon bark which had been sent to us from the islands of Celebes and Timor, their respective producing districts, when anatomically examined by Dr. Giessler proved to be identical, the parent-plant of both, according to this authority, being *Cinnamomum Burmanni*, Blume (*C. Kiamis*, Nees), N. O. Lauraceæ.

¹⁾ Comp. also camphor oil, p. 27.

Distillation yielded us 0,5% of a brownish-yellow oil with an aroma resembling that of Ceylon cinnamon oil, but less delicate. The constants of the oil also differed from those of Ceylon cinnamon oil, being: $d_{15.0}$ 1,0198, $n_D^{20.0}$ 1,58282, soluble in 0,8 vols. 80% alcohol and more; giving no clear solution with 10 vols. 70% alcohol. The cinnamic aldehyde content, as determined with neutral sodium sulphite, was 77%, while a determination with bisulphite showed about 80%, but in the latter case the result was very untrustworthy, probably owing to the fact that other aldehydes were also present, and that their bisulphite-compounds separated out from the solution and prevented an accurate reading. The determination of phenols with 3% soda liquor gave a phenol-content of about 11%. Unfortunately part of the oil had become emulsified during the shaking with the soda liquor, hence it was impossible to read off accurately those parts of the oil which had not entered into reaction. The value given above is therefore only approximate.

Oil of *Matricaria discoidea*. Among the numerous plants of the N. O. Compositæ which have been introduced among us from North America is *Matricaria discoidea*, D. C., a plant resembling our chamomile, but smaller and also particularly differing from our chamomile in having much smaller marginal flowers. The plant was introduced into Europe in the middle of the 19th century and has acclimatised itself with surprising rapidity; being, for instance, very common in Württemberg and in many parts of Alsace-Lorraine, in particular in the neighbourhood of railway-stations¹⁾. We have also observed this chamomile in Leipzig and its vicinity (Railway Station to Berlin, Gohlis, Eutritzsch, Rosental, Schönefeld, Zwenkau, and Miltitz), and have caused a small quantity of it to be collected locally for distilling purposes. From the entire plant, every part of which appears to contain essential oil, we obtained 0,15% of a dark-brown oil, studded with paraffin crystals when at ordinary temperature, possessing an odour which may be said to be intermediate between that of common and of Roman chamomile oil. Sp. gr. at 30° 0,9175, acid v. 18,7, ester v. 77,5. On account of its fairly considerable paraffin-content the oil made no clear solution even with 90% alcohol. The paraffin which was separated out, after being twice recrystallised from dilute alcohol, melted between 58 and 61°.

Oil of *Meriandra benghalensis*. In the course of the present year we received from the Government of the Italian colony of Eritrea two essential oils prepared in that colony, and described as sage oils. The samples were of a pale-brown colour and possessed an odour which, although it bore some resemblance to that of sage oil, was nevertheless

¹⁾ According to a symposium in the *Pharmakognostische Rundschau* for the year 1910 (published by Mittlacher, Tunmann and Winkel), Vienna 1911, p. 85.

clearly different. Moreover, the sp.gr. of the two samples was higher than that of sage oil; and they also differed from that oil in being lævotatory. At our request a sample of the distilling-material had been forwarded with the second oil-sample, and we were therefore in a position to have the raw material botanically examined. Dr. Giessler ascertained that the plant from which the oil was distilled does not belong to the genus *Salvia* at all, but is, in fact, *Meriandra benghalensis*, Benth.; N. O. Labiatae (recently re-named *M. dianthera*, Briq.), the leaves of which, as a popular remedy, are used for similar purposes as those of sage. Upon distilling the raw material it yielded us 1,5% of a pale brown oil, with an odour reminding both of sage and of rosemary. Further examination produced the following results: d_{150} 0,9513, $\alpha_D - 2^\circ 5'$, n_{D200} 1,47490, acid v. 3,7, ester v. 14,8, soluble in 2 vols. and more of 70% alcohol. When placed in a freezing mixture the oil solidified to a butter-like consistency as a result of the separation of camphor.

The two oils distilled in Eritrea behaved as follows:

1. d_{150} 0,9464, $\alpha_D - 0^\circ 30'$, n_{D200} 1,47176, acid v. 1,0, ester v. 11,8, sol. in 2 vols. a. m. 70% alcohol.
2. d_{150} 0,9526, $\alpha_D - 1^\circ$, n_{D200} 1,47548, acid v. 5,6, ester v. 9,3, sol. in 1,8 vols. a. m. 70% alcohol.

Neither sample possessed its full camphor-content, for in the preparation of No. 1 part of the camphor had separated out during distillation in the condensing worm, while from No. 2 it had been partly extracted by freezing-out. In both cases, samples of the separated camphor had been sent to us from Eritrea, and the substance was identified more closely from its m. p. (176°), and its oxime (m. p. $118,5^\circ$). Optical examination showed it to consist of the dextrorotatory modification.

Santolina Oil. *Santolina Chamæcyparissus*, L., N. O. Compositæ, is a native of Southern Europe, and is much cultivated as a garden-plant. It is distinguished by its powerful, penetratingly aromatic odour. Formerly it was official on account of its therapeutic properties, among others as an antispasmodic and anthelmintic, and to this day it is used as a popular remedy throughout its native region. A sample of the herb received from Turin has been worked up by us for essential oil, of which it yielded 0,47%. The oil was of a dark-brown colour and in its odour reminded somewhat of wormwood, or rather of tansy. d_{150} 0,9065; n_{D200} 1,50040; acid v. 6,6, ester v. 16,4; ester v. after acetyl. 74,2; opt. rot. impossible to determine on account of the dark colour. The oil was soluble in 0,5 vols. a. m. 90% alcohol, with elimination of paraffin; insoluble in 80% alcohol. So far no further particulars of its composition have been ascertained, but judging from the odour, thujone appears to be one of the constituents.

Santolina oil has also been mentioned recently in a French periodical¹⁾, but no particulars of its properties are given there, all that is stated being that the oil has an odour reminding of ambrette and closely resembling that of muscatel sage oil. We cannot say the same of the oil distilled by us.

Oil of *Satureja cuneifolia*. We are indebted to Dr. Giaconi, of Trieste, for four samples, distilled by himself in Dalmatia, of oil of *Satureja cuneifolia* Tenore, N. O. Labiatae. The oils were of a brownish-yellow colour and possessed an odour reminding of thyme; their other characteristics were as follow: —

	d_{40}	n_D	$n_{D_{40}}$	Phenols	Soluble in
1.	0.9182	— 4° 45'	1.49816	28%	1.2 vol. a. m. 80% alc.
2.	0.9190	— 5° 15'	1.49824	34%	1.1 vol. a. m. 80% alc.
3.	0.9444	— 2° 15'	1.50528	59%	2.5 vol. a. m. 70% alc.
4.	0.9440	— 1° 50'	1.50556	59%	2.7 vol. a. m. 70% alc.

Samples nos. 1 and 2 were insoluble in 10 vols. 70% alcohol, nos. 3 and 4 were soluble in about their own vol. of 80% alcohol. The phenols consisted of carvacrol, the non-phenols had a pronounced odour of cymene, but the samples at our disposal were too small to prove the presence of that body.

New Pharmacopœias. German Pharmacopœia V.

In our criticism of the articles mentioned in the 5th edition of the German Pharmacopœia which relate to our branch of industry, we pointed out, *inter alia*, how regrettable it was that the draft of the Pharmacopœia had not been submitted to public comment at the time, because, had it been so submitted, many incorrect statements might have been rectified before publication of the book. A paper read by Prof. Kobert before the Rostock Medical Society in the spring of the present year shows that we did not stand alone in expressing this view. In this paper, of which an abstract has appeared in the *Pharmazeutische Zeitung*²⁾, Prof. Kobert points out that it would be desirable, for critical as well as for other reasons, "if the mystery-mongering which was unfortunately still regarded as necessary in the preliminary work of the Pharmacopœia were done

¹⁾ *Parfum. moderne* 4 (1911), 97.

²⁾ *Pharm. Ztg.* 36 (1911), 381.

away with once and for all". If all the proceedings of the Committees were always published immediately, criticism could make itself heard before the publication of the Pharmacopœia and would be able to cause a great many things to be altered which are now immutably fixed for a decade. It is to be hoped that such well-founded complaints will find consideration in authoritative quarters.

In his lecture Kobert also makes mention incidentally of methyl salicylate, which has unfortunately been disregarded by the Pharmacopœia Council in Germany, and has not been made official, whereas elsewhere, for instance in Britain, it is very popular. Methyl salicylate is suitable both for internal administration (in capsules) and for external use; it is a favourite antiseptic mouth-wash (in 1 to 5% alcoholic solution). As it represents the pure ester, and is much cheaper than natural wintergreen oil, as a constituent of which it was first discovered, Kobert regards it as unpractical that many dentists should still continue to prescribe "*Oleum Gaultheriæ*", the natural oil, in lieu of the artificial preparation.

On the chlorine test of benzaldehyde prescribed by the German Pharmacopœia V, see p. 119.

Dutch Pharmacopœia.

A supplement to the 4th Edition of the Dutch Pharmacopœia¹⁾, dated July 1910, has made its appearance. In this Supplement newly-admitted preparations are described and incorrect statements which have appeared in the Pharmacopœia itself are corrected. Among these corrections are some which relate to essential oils, and these we quote below: —

Lavender Oil: The maximum limit of value of the sp. gr. which was previously 0,890, has been raised to 0,895.

Rosemary Oil: The Pharmacopœia requires rosemary oil not to rotate above $+15^{\circ}$ in a 2 dm.-tube. This error has now been removed, the Supplement stating (which is correct), that the requirement applies to a 1 dm.-tube.

Turpentine Oil, purified: The prescription dealing with the preparation of the oil has been revised in this respect that the proportion of the oil used which must distil over is no longer fixed exactly at $\frac{3}{4}$ of the whole, but at "about" that figure.

The endeavour of the Pharmacopœia Council to remove officially any errors and mistakes contained in the Pharmacopœia, which is finding expression in the publication of such Supplements, deserves high commendation. It would be desirable that very many Pharmacopœia Councils would follow the Dutch example.

¹⁾ Comp. the review in our Report of October 1906, 84.

Chemical Preparations and Drugs.

Benzoin, Siam. The acute scarcity which prevailed some months ago in this article, which is one of such great importance in the perfumery industry, has been removed for the time being by the arrival of some large parcels. Benzoin in fine, bold almonds, which is one of our specialities, is, however, as yet by no means plentiful, and it has therefore been impossible up to the present to reduce the quotations for this quality to the level which might have been expected in view of the weaker market.

Benzyl Acetate, free from chlorine. This excellent odoriferous body is steadily acquiring greater importance and its cheapness has secured an opening for it everywhere, particularly in perfumes of moderate price. The inferior qualities which are often offered at low prices by other firms, and to which we have drawn attention on more than one occasion, are still met with from time to time, and we therefore think it necessary to point out that a pure, chlorine-free benzyl acetate, such as we supply, should answer the following requirements: d_{15}^0 1,060 to 1,062, α_D^{20} 0, n_{D20}^0 1,502 to 1,504, ester-content 98 to 100%, soluble in about 6 volumes and more 60% alcohol and in about 2 volumes and more 70% alcohol. The product must be free from chlorine-compounds.

We shall be pleased to supply samples of our benzyl acetate free upon application, in order to enable comparisons to be made with samples offered at lower prices.

Citral. As is well-known, this article is prepared from lemongrass oil, and in view of the fact that for some considerable time past the raw material has only been obtainable in sufficient quantities by conceding enhanced prices, it has been necessary also to advance the quotations of citral. This advance will probably be more than a merely temporary one, for owing to over-production the selling prices of citral have long ago ceased to stand in proper relation to the cost price of lemongrass oil, and an equalisation of the difference would now be desirable.

Civet. Although supplies of really fine quality were not always available, there has been no increase in the prices, because the demand has not been particularly brisk. There should, however, be no chance of a reduction in the quotations from the present level.

According to a by no means very exhaustive report by the British Consul at Adis Abeba¹⁾, civet cats are kept in Western Abyssinia. Once every nine days the odoriferous substance is extracted from the animal, the yield averaging about one Wagia (26 g.) of civet each time. The extraction takes place in the presence of the buyer, who, says the Consul, "immediately proceeds to adulterate the civet with butter." In this condition the article is sold in Mohammedan districts, such as Jimma, Om-

¹⁾ Diplomatic and Consular Reports, 1911, Annual series, No. 4759.

durman and Aden. The selling-prices at Adis Abeba and at Gore are about equal to $1\frac{1}{2}$ dollars per Wagia. There can be no doubt that this does not refer to the quality which is used in Europe for perfumery-purposes, for such prices would of course be out of the question here. The report, in fact, goes on to say that in addition to the above a certain quantity of civet is manufactured which is suitable for perfumery purposes, but that it is extremely difficult, and requires considerable practice, to detect the adulterations. We only reproduce this communication here because reports concerning civet reach us so rarely from the producing districts, and because the Consul's statements indicate that probably by far the larger part of the civet which is produced in Abyssinia is brought into commerce in an adulterated state. As it is very difficult to detect admixtures of butter in civet, it is desirable to purchase the last-named article only from sources of proved trustworthiness, and to look upon the price as a matter of only secondary importance.

Coumarin. The consumption of this important odoriferous substance is still growing. The price has undergone no change within the past few months, although cutting of the convention rates (which are low enough in all conscience), is still a matter of frequent occurrence. These cheap offers, however, mostly relate to qualities which are too dear even at such apparently advantageous figures.

Following our previous communications on tonca-beans containing coumarin, we quote from a British Consular Report¹⁾ the statement that the parent-plant of this drug (*Dipterix odorata*, Willd.; N. O. Leguminosæ), grows on the southern banks of the Orinoco in Venezuela. Monkeys eat the fruit, but spit out the seeds. The latter are collected, steeped in spirit, dried, and exported principally to the United States and Germany, where they are used in the tobacco industry. The bulk of the tonca-beans are taken from Ciudad Bolivar to Trinidad, whence they are shipped further.

On the action of coumarin as a fish-poison see p. 124.

Geraniol. Notwithstanding the fact that our facilities for producing pure geraniol are unsurpassed in magnitude, we were not always able throughout the past summer to give punctual delivery, so exceptionally brisk was the demand. The principal reason of this is of course the scarcity of all varieties of geranium oil, for since such excessive prices have been asked for, say, African geranium oil, a large number of perfumers have become regular buyers of geraniol. The upward movement in the rose-oil market has naturally also contributed to stimulate the demand for geraniol, for it is unfortunately impossible to prevent considerable parcels of geraniol reaching the sophisticators of rose oil in Bulgaria and elsewhere by roundabout ways. As we are occasionally

¹⁾ Diplomatic and Consular Reports 1911, No. 4758, p. 9.

asked for geraniol from palmarosa oil, we take this opportunity of stating that since we have succeeded in utilising other material for preparing geraniol of the high degree of purity now reached, we have quite given up the costly process of preparing geraniol from palmarosa oil.

Heliotropin. Thanks to our exceptionally favourable position as manufacturers of safrol, the raw material from which heliotropin is made, we have been able to extend the manufacture of this product very considerably, and we are now in a position to avail ourselves of all the advantages which accrue from our ability to manufacture on a large scale. Our product is distinguished by the excellence of its perfume, and is free from the so-called "chemical odour" of so many competing heliotropins, while the competing preparations, although offered at lower prices, may be left out of account so far as the manufacture of high-class perfumes is concerned.

Menthol. As usual, we deal with this article under the heading of "Peppermint Oil, Japanese", see p. 70.

A. Knick and J. Pringsheim¹⁾ have ascertained that when dogs are given 0,2 g. menthol daily internally per kilo weight of the animal, their bile acquires a disinfecting action capable of destroying, or at any rate arresting the development of, the germs of typhus fever.

The favourable action of menthol on ulcers, and in catarrhs and other infectious diseases which has been observed by Laurens²⁾ is probably due to the disinfecting powers of this alcohol.

Musk, Tonquin. Nothing of special interest is to be reported concerning this important article, the trade in which, as our friends know, is one of those special subjects to which we pay exceptional attention. The table below shows that the exports via Shanghai have been rather considerable, and it only remains to be added that during the period covered by this Report the prices of the best qualities have remained unaltered.

Exports of Musk from Shanghai in the first six months of 1911.

Year	to Paris	to London	to New York	to Germany and Austria	Total
	Catties	Catties	Catties	Catties	Catties
1911	376	147	312	20	855
	compared with				
1910	342	140	226	55	763
1909	430	59	151	50	690
1908	578	16	155	9	758
1907	649	36	269	37	991
1906	581	—	177	45	803

¹⁾ Deutsch. Arch. f. Klin. Med. 101 (1910), 137. Quoted from Therap. Monatsh. 25 (1911), 338.

²⁾ La Clinique, 17. February 1911. Quoted from Journ. de Pharm. et Chim. VII. 3 (1911), 460.

Peru Balsam. As usual there is very little new to report concerning this article. Thanks to the clever manipulation of the market on the part of the Hamburg firms which control the imports, the prices have been maintained at their previous level, and at the moment from *M* 16.— to *M* 16.50 per kilo has to be paid for balsam of unimpeachable quality in the first hand. In spite of this, the price-cutting in so-called "German Pharmacopœia V-quality" continues unchecked! It remains a truism that it is impossible to forecast the future of the article, for all information from the district of collection is deftly suppressed; we have some suspicion, however, that no lower prices are to be expected for some time to come.

Among the German Pharmacopœia (V) tests for Peru balsam is one for fatty oils, in which it is laid down that 1 g. Peru balsam must dissolve clearly in a solution of 3 g. chloral hydrate in 2 g. water. According to Stöcker¹⁾, however, unquestionably pure balsams do not always give an entirely clear solution in the proportions prescribed by the Pharmacopœia-test, and it is therefore preferable to use 3,5 g. chloral hydrate instead of the 3 g. there demanded. G. Fromme²⁾ has observed that in the case of pure balsams this turbidity ensues when the chloral hydrate is not quite dry, the water which is present in the last-named substance preventing a clear solution. Moreover, it happens sometimes that the solution is rendered turbid by mechanical impurities, and Fromme therefore recommends that when the balsam is not quite pale it should be filtered before the test is applied; also that only absolutely dry chloral hydrate, which has been kept in a lime-box, should be employed.

Pollantin. The summer which is now drawing to a close has been remarkable as a season of abnormal drought, which set in early, and which has made it a period of serious suffering for persons subject to hay-fever. Hence our hay-fever serum pollantin has experienced a brisk demand, considerably surpassing that of the previous year.

This season we have supplied a few hay-fever patients experimentally with a new pollantin-preparation known as "pollantin ointment", and judging from the reports which have reached us, this preparation has been very well received, and has fully justified expectations. As a result of the success of this experiment we intend to place the ointment upon the market in the coming spring, and to publish particulars of the remedy in our Report of April 1912. We also hope then to be able to report the result of successful experiments made in combatting the troublesome complaint of hay fever-asthma, with which so many patients are afflicted towards the end of the hay-fever season.

We beg to inform our business friends, especially the chemists among them, that we are prepared to exchange old tins of liquid Pollantin bearing

¹⁾ Apotheker Ztg. 26 (1911), 283.

²⁾ Quoted from the Annual Report of Caesar & Loretz in Halle o. S., end of August 1911, 14.

control numbers below 153 inclusive for fresh ones. We therefore beg them to search for such numbers and send them to our Branch Office, when the new tins will be forwarded in due time next spring, unless prompt return is demanded expressly. Powdered Pollantin is of unlimited keeping quality and therefore is not taken back again.

Rose "Schimmel & Co." (Red Rose). In referring to German rose oil on p. 75 of the present Report, we laid stress upon the fact that we have this season been compelled to make it our chief object to prepare a sufficient quantity of the natural basis of the above-mentioned new speciality. To have fully achieved this object, in spite of the unfavourable circumstances, has been for us an ample recompense for the disappointments which the present year's crop of roses in Miltitz has brought us. Our "Red Rose" has gained the goodwill of experts in every country where delicate rose-perfumes are appreciated, and we can hardly recall so striking a success with any other of our specialities in this line. The scent of the preparation is so perfect and so delicately reproduced that in most cases it is possible to use the "Red Rose" by itself, without any addition of other perfumes and oils. It is true that we have made preparations to cope with a considerable demand during the season now before us, but all the same we feel bound to impress upon our friends that this perfume, with its natural basis, cannot be manufactured at will throughout the seasons, and to suggest to them that they should bespeak their requirements in good time.

Safrol has throughout been in great demand, hence, when large and cheaper supplies of crude camphor oil came to hand from Japan there was no need for more than a slight reduction in the price. A brisk business, more particularly for future delivery, then developed, and as a result of this a large portion of our output has been disposed of. We produce this article on such a large scale, however, that we are able to meet any pressure which may be put upon our manufacturing-powers.

Thymol. No alteration worth mentioning has taken place in the position of the thymol market during the summer-months, for the heavy stocks of this preparation, which stand in cheaply on the basis of a cost-price of 8/- per cwt. for ajowan seed, have not yet been cleared. Rather there are complaints of the generally listless character of the business in thymol, and even the fact that in the meantime the price of the raw material has risen to about 9/6 per cwt. has so far failed to react upon the thymol-prices. Not until some of the principal price-cutters are growing tired of further competition will there be any possibility of an improvement in the position. The imports of ajowan seed via Hamburg up to the end of August of the present year only amounted to about 7850 bags, as compared with 25500 bags in the corresponding period of the year 1910.

Notes on Scientific Research in the Domain of the Essential Oils.

General.

In an article entitled "La chimie des parfums en 1910", P. Jeancard and C. Satie¹⁾ briefly review the work which has been published in the year 1910 in the domain of the terpenes and essential oils.

A part of Rabak's essay on the manufacture of essential oils in the United States of America, to which we referred in our last Report²⁾, has now been published in the *Journal of the American chemical Society* [Vol. 33 (1911), p. 1242].

Analytical Notes.

In the report on our investigations into the detection of artificial esters in bergamot oil³⁾ we described a method of testing for terpinyl acetate based upon the shorter time required for the saponification of linalyl acetate as compared with terpinyl acetate. Two tests were to be made by the same method, and after saponification extending over $\frac{1}{2}$ and 1 hour respectively the ester value was to be determined, and the presence of terpinyl acetate to be concluded, from a possible difference between the two readings. A short table was given showing the differences which had been found by us in the pure esters as well as in pure bergamot oil and in bergamot oil adulterated with terpinyl acetate. An addition of 5% terpinyl acetate to pure bergamot oil still showed a difference in the two ester values of 3.5, but no smaller addition could be detected with certainty, because the difference became too slight and fell within the limits of possible error.

Now, since more heavily adulterated oils would already arouse suspicion on account of their constants, and as additions of less than 5% terpinyl acetate would only slightly affect the oil in question, we were anxious so to improve the method so that it could be employed to detect positively smaller adulterations than that stated above.

After many experiments we have found the method described below to be more accurate and we therefore publish it here in completion of our previous statements.

Four separate tests should be made with samples accurately weighed in the saponification flask (2 cc. each is a suitable quantity). The oil is then mixed with about 5 cc. alcohol and a few drops of alcoholic phenol-

¹⁾ Rev. gén. de Chim. 14 (1911), 177. From a reprint kindly sent to us.

²⁾ Comp. Report April 1911, 146.

³⁾ Report October 1910, 60.

phthaleine solution (1:100) and the acid estimated by titrating with semi-normal potash liquor¹⁾. Next, the contents of two of the flasks, with an addition of 10 cc. seminormal potash liquor are saponified during 1 hour on the water-bath by the familiar method. The contents of the third flask are boiled for 2 hours with 20 cc. liquor and those of the fourth flask are diluted with 25 cc. neutral 96% alcohol and saponified during 1 hour with 10 cc. liquor. At the end of the boiling the four samples should be cooled down quickly and equally by immersion into cold water and titrated immediately.

In the case of pure bergamot and lavender oils the difference in the ester values between the two-hours' and the one-hour's diluted sample amounted to 3, or at most 4, whereas the ester values of the two normal saponifications represented about the mean of these figures. If terpinyl acetate is added to the oil the difference becomes correspondingly greater, the ester value of the two-hours' saponification being increased in proportion to the contents, whereas that of the sample diluted with alcohol only increases slightly. The ester value of the two normal saponifications always remains at about the mean of the two others. The subjoined table shows the values found by us for a pure bergamot oil and for the same oil after adding the stated quantities of terpinyl acetate:

Seminormal Potash liquor:	10 cc.	20 cc.	10 cc. + 25 cc. alc.	Difference between Cols. 2 and 3
Time of saponification:	1 hour	2 hours	1 hour	
Bergamot oil, pure . . .	99,7	100,5	97,4	3,1
+ 2% Terpinyl acetate	102,1	104,5	98,1	6,4
+ 4% " "	103,3	108,1	98,1	10,0
+ 6% " "	105,7	112,2	98,6	13,6
+ 8% " "	107,0	114,4	98,4	16,0
+ 10% " "	108,6	118,1	99,1	19,0
+ 15% " "	113,4	126,7	101,0	25,7
+ 20% " "	118,0	135,6	101,3	34,3

It follows from the above that an addition of 10% terpinyl acetate produces a difference in the ester values of 19 (5,5 according to the

¹⁾ Report April 1911, 69.

former $\frac{1}{2}$ h. and 1 h. saponifications), and that an addition of only 2% produces a difference of 6,4; consequently even small sophistications of this nature should now be readily traceable.

A remarkable fact is that when up to about 10% terpinyl acetate is added the ester value of the diluted sample is only slightly increased, the true linalyl acetate content being thus ascertainable with approximate exactitude.

In connection with the above we give the analytical values of a few samples of adulterated bergamot oil which have been submitted to us for our opinion: —

d_{150}	0,8955	0,8827	0,8848
α_D	+ 16° 10'	+ 9° 0'	+ 19° 25'
Evaporation-residue	4,2%	4,8%	6,8%
Sap. v. of evap. residue	180,0	186,6	178,7
Solubility in 90% alcohol	0,3 v. a. m.	0,3 v. a. m.	0,3 v. a. m.
Acid v.	1,8	1,6	4,1
Ester v. after 1 hour's saponif. with 10 cc. seminormal potash	104,2	96,4	97,4
Ester-content (calc. as linalyl acetate).	36,5%	33,7%	34,1%
Ester v. after 2 hours' saponif. with 20 cc. seminormal potash	121,8	105,6	101,3
Ester v. after 1 hour's saponif. with 10 cc. seminormal potash + 25 cc. alcohol	88,2	86,6	92,1
Difference	33,6	19,0	9,2
Sap. v.	106,0	98,0	101,5
Acid v. II	102,3	88,7	92,0
Difference	3,7	9,3	9,5
Terpinyl acetate content	about 20%	about 10%	about 4%
Esters of sparingly volatile acids } Glycerol esters }	not found.		

The dilute saponification indicates a content of linalyl acetate

below 30,9%	about 30,3%	about 32,2%
instead of above 36,5%	33,7%	34,1%

While on this subject we may refer to a notice by Jeancard and Satie¹⁾ on the estimation of citric esters and glycerol esters in essential oils. These authors isolate the citric acid from the saponified oil by a suitable method and detect the crystals by means of the microscope. The glycerol they convert into acroleine with acid sulphate of potash.

¹⁾ Rev. gén. de Chim. 14 (1911), 177.

An important benzaldehyde-test is that for the presence of chlorine-compounds, and for this reason it has been incorporated in the new Edition of the German Pharmacopœia among the tests prescribed for this article. The Pharmacopœia reference is as follows (p. 73): "When a small piece of folded filtering-paper is saturated with 1 g. benzaldehyde, burnt in a porcelain dish under a large glass beaker, the inside of which has been moistened with water, and the contents of the beaker, after combustion, are rinsed out with a little water and poured on a filter, the filtrate, when acidulated with nitric acid, must remain clear upon the addition of a silver nitrate solution".

This method has been criticised by J. Herzog¹⁾ at the March meeting of the German Pharmaceutical Society. According to Herzog's experience it is very difficult to carry out the test when the method of the Pharmacopœia is adhered to closely. "The reaction", he said, "will either give no result at all, or will be effective only with benzaldehydes containing an abnormally large proportion of chlorine". Herzog found that an addition of 5 drops chlorobenzene to 5 g. benzaldehyde only gave the faintest possible chlorine reaction when the test was carried out in accordance with the Pharmacopœia requirements, and that an addition of only 2 drops of chlorobenzene to 5 g. benzaldehyde could not be detected at all by this method. His explanation of the non-reaction is that complete combustion of the paper soaked in 1 g. benzaldehyde makes the beaker so hot that the water adhering to its sides, and with it any hydrochloric acid which may have been absorbed, is eventually completely evaporated, and that the hydrochloric acid is thus lost for the purposes of identification. In order to obviate this trouble Herzog recommends that instead of 1 g. only 0,2 g. benzaldehyde (he himself uses 4 drops) be burnt each time, for when this is done the beaker is not overheated and its contents remain moist. With the two mixtures referred to above Herzog obtained a heavy precipitate in one case, and a noticeable precipitation of silver chloride in the other.

As we also feel ourselves entitled to express an opinion on the subject of the chlorine test for benzaldehyde, we wish to point out that we are unable to endorse Herzog's proposal without reservation, because when such a small quantity of benzaldehyde is used as is recommended by Herzog, the limit of sensitiveness of the reaction is also reduced. And this is a most material consideration, for in most examinations the question at stake will not be whether the benzaldehyde contains a greater or smaller proportion of chlorine but, whether or not it contains traceable proportions of chlorine at all. Therefore, when following Herzog's advice and using only 0,2 g. aldehyde, a benzaldehyde may in certain circumstances be pronounced to be chlorine-free which when tested

¹⁾ From the Report of the Meeting in the *Berichte d. deutsch. pharm. Ges.* **21** (1911), 202.

by the method described below will be found to contain chlorine. This we have proved absolutely by comparative tests. Herzog is right in criticising the wording of the Pharmacopœia-method, which should have been much more explicit, for as it is at present it may lead first to misunderstandings and subsequently to such unsatisfactory results as have been obtained by Herzog. But when this test is carried out in a proper manner it is so extraordinarily delicate that it will indicate even the smallest traces of chlorine-products. In the course of many years we have arrived in our laboratory at the following method of examination²⁾: —

“A piece of filtering paper measuring about $2 \times 2\frac{1}{4}$ in., and folded in the shape of a spill, is saturated with the oil, the excess of oil is thrown off and the paper is placed in a small porcelain dish which in its turn reposes in a larger dish, measuring about 8 in. in diameter. The paper is now ignited, and a beaker of a capacity of about 2 litres, moistened inside with distilled water, which has been held in readiness, is quickly placed over the paper. The respective sizes of the implements used must be such that the rim of the larger dish must stand out well all round from the beaker. After the flame is extinguished the beaker should be left in position for about one minute, after which the products of combustion which have been deposited against the moist sides of the beaker are rinsed out with a little (10 cc.) distilled water, and poured upon a filter. The filtrate, acidulated with a drop of nitric acid, must remain clear when silver nitrate solution is added.”

When this method is followed the test is extraordinarily sensitive, 1 drop of monochlorobenzene in 50 g. benzaldehyde (that is to say a very much weaker solution than that used by Herzog), and an even smaller proportion of chlorine being detected without any difficulty, while the same solution when tested by Herzog's method in the presence of a very minute proportion of chlorine in the benzaldehyde was either uncertain or gave a negative result. This is quite natural, because in the last-named case less benzaldehyde is burnt up than with our method. Another advantage of our method is that practically no paper is burnt, the only body which goes into combustion being benzaldehyde. Experiments have shown us that many filtering papers contain traces of chlorine, and when therefore the paper is burnt up completely (as required by the German Pharmacopœia) it is quite possible that a faint chlorine-reaction will make its appearance, which might erroneously be attributed to the faulty condition of the benzaldehyde. We have frequently tried this experiment in our laboratory. We desire to point out further that the beaker does not become heated to any extent if our method is strictly adhered to.

²⁾ Gildemeister and Hoffmann, *Die ätherischen Öle*, 2nd Ed. Vol. I. p. 630.

Many years ago we criticised the citral estimation with hydroxylamine hydrochloride described by Walther¹⁾, which at the time gave no good results when we submitted it to a control-test. Neither did the alteration proposed by Bennett²⁾ lead to any satisfactory results. According to H. C. Fuller³⁾, it is possible to use the hydroxylamine method for estimating the camphor-content of spirits of camphor. He dilutes 25 cc. spirits of camphor with 2 g. carbonate of sodium in a 100 cc. flask. Next he adds from a burette 35 cc. of a solution of 20 g. hydroxylamine hydrochloride in 30 cc. water and 125 cc. absolute alcohol free from aldehyde. The mixture is heated for two hours in a reflux-condenser to a gentle boiling-temperature, cooled down to 25°, diluted with a mixture of 6 cc. hydrochloric acid (sp. gr. 1,12) and 6 cc. water and again diluted to half a liter. The free mineral acid is then neutralised in 55 cc. of this liquid, methyl orange being employed as an indicator, after which phenolphthaleine is added, and the hydroxylamine hydrochloride is titrated back with decinormal soda liquor. At the same time a blank test is prepared. The difference between the two titrations corresponds to the quantity of camphor oxime which has been formed. 1 cc. decinormal soda liquor = 0,01509 g. camphor. No particulars are given of any results obtained by this method, and a control-test made by us has given no satisfactory results.

In our last Report we made mention of a method for the determination of hydrocyanic acid described by L. Rosenthaler⁴⁾ and based upon the conversion of this acid by means of mercuric chloride into mercuric cyanide and hydrochloric acid. Another method devised by the same author⁵⁾ is based upon the conversion of hydrocyanic acid with mercuric nitrate, according to the equation: $\text{Hg}(\text{NO}_3)_2 + 2\text{HCN} = \text{Hg}(\text{CN})_2 + 2\text{HNO}_3$. The excess of mercuric nitrate is titrated with ammonium sulphocyanide solution (using ammonium ferrisulphate as an indicator). For this determination a decinormal mercuric nitrate solution, a decinormal ammonium sulphocyanide solution, and a saturated ammonium ferrosulphate solution slightly diluted with nitric acid are required. The liquid containing hydrocyanic acid is allowed to run into the excess of solution of mercury, whereupon the titrating-vessel is closed and vigorously shaken. Whether sufficient mercuric nitrate has been added is shown by the absence of hydrocyanic acid odour in the liquid. Saturation of the liquid with chlorine-free alkali nitrate produces more clearly-defined reactions. 1 cc. decinormal $\text{Hg}(\text{NO}_3)_2$ = 2,7018 mg. HCN.

¹⁾ Pharm. Zentralh. 40 (1899), 621; 41 (1900), 614; Report April 1900, 22; October 1901, 26.

²⁾ Comp. Report April 1900, 110; October 1900, 153.

³⁾ Oil, Paint and Drug Reporter 80 (1911), No. 7, p. 39.

⁴⁾ Report April 1911, 153.

⁵⁾ Arch. der Pharm. 249 (1911), 253.

This method is not adapted for the determination of hydrocyanic acid in the presence of benzaldehyde cyanohydrin.

On estimating the peroxide-content of turpentine oil see p. 93.

Physical Notes.

Chr. J. Hansen has published a further contribution to the polemics between himself and von Rechenberg, under the title of "A Final Reply" [*Zeitschr. f. physik. Chem.* **76** (1911), 753]. The publication contains no new facts.

Auwers and Eisenlohr¹⁾ have continued their spectro-chemical investigations to which we referred in our October Report of last year²⁾. They have examined bodies with one pair of conjugated double linkings as well as others with multiple connected conjugations. In order to make distinction easy between the different varieties of the multiple conjugation, they have given to a continuous chain of conjugated double linkings, such, for example, as $—C=C—C=C—C=C—$, the name of "accumulated conjugation" while systems such as $—C=C—C=O$ are called "crossed

conjugations." The whole of the material has been calculated with the aid of the new atomic refractions drawn up by Eisenlohr³⁾, and the values given in the first paper have also been calculated anew. The term "exaltation of the specific (molecular) refraction and dispersion" has been replaced by the term "specific (molecular) exaltation" ($E\Sigma$). This value, $E\Sigma$, has been calculated for a large number of combinations, both from personal observations and from data ascertained by others. Although apparent contradictions were occasionally noticed, further investigation almost invariably revealed the fact that there is nowhere an absence of rules, notwithstanding the somewhat complicated nature of the optical characteristics of bodies with accumulated and crossed double bonds.

We are unfortunately precluded from want of space to enter into the details of this valuable experimental material and are compelled to refer for such particulars to the original paper.

Ciamician and Silber⁴⁾ have continued their researches⁵⁾ into the chemical action of light, upon which we have already commented several times. They purified the trimeride of benzaldehyde⁶⁾ which they had

¹⁾ Journ. f. prakt. Chem. II. **84** (1911), 1.

²⁾ Comp. Report October **1910**, 164.

³⁾ Zeitschr. f. phys. Chem. **75** (1910), 585. Comp. Report April **1911**, 155.

⁴⁾ Berl. Berichte **44** (1911), 1559.

⁵⁾ Report October **1907**, 123; October **1909**, 159; October **1910**, 167.

⁶⁾ Comp. Report October **1909**, 161.

obtained upon a previous occasion by recrystallising from methyl alcohol, and from the mother-liquor they obtained an isomeric trimeride, m. p. 144 to 145°.

Cinnamic aldehyde, after having been exposed to light in a glass tube for twelve months, formed a brown, transparent resinous mass, from which a polymeride consisting of a white resinous mass, m. p. 115° (after previously dripping together at 103°) could be isolated. Determination of the molecular weight produced no uniform results; values were obtained fluctuating, according to the solvent, between $(C_9H_8O)_4$, $(C_9H_8O)_5$ and $(C_9H_8O)_{10}$.

H. Malosse¹⁾ has determined the specific rotation of camphor dissolved in acetone. With a concentration of 40,7413% the values are $[\alpha]_{D13.7^\circ} + 50,549^\circ$; the rotation is at its minimum with a percentage of 8,4604 ($[\alpha]_{D14.3^\circ} + 48,709^\circ$) and gradually increases to $[\alpha]_{D23.2^\circ} + 50,070^\circ$ with a percentage of 1,0684.

On the equilibrium benzaldehyde + hydrocyanic acid $\rightleftharpoons$ benzaldehyde cyanohydrin, see p. 19.

Pharmaco-physiological Notes.

In our last Report²⁾ we commented upon a paper by Coupin on the influence of certain volatile bodies upon the development of germinating grains of cereals. Since then the author³⁾ has extended his investigations over a series of essential oils, and has come to the conclusion that these oils may be divided into five groups.

Group 1 consists of oils which immediately destroy the young plants, *viz.*, oils of niaouli, star anise, and Russian and French anise.

Group 2 comprises those oils which only kill the plants after a certain time, *viz.*, oils of thyme, wild thyme, sassafras, lavender, wormwood, spike, bergamot, neroli, juniper berries, spiræa, mace, tansy, and rosemary.

Group 3 embraces the oils which retard the development of the plants and cause them to become more or less withered, *viz.*, oil of cedro, verbena, Ceylon cinnamon, cajuput, sweet fennel, cassia, ylang-ylang, *Chione glabra*, mandarin, coriander, hyssop, sage, chamomile, eucalyptus, rose (Turkish), wintergreen, balm, peppermint (Paris), peppermint (American), geranium (French), angelica, caraway, and bitter orange.

Group 4 contains the oils which retard the growth of the plants, *viz.*, oil of citronella, bitter fennel, cumin, sweet orange (Calabrian), origanum, E. I. sandalwood, and orris.

¹⁾ Compt. rend. 153 (1911), 56.

²⁾ Report April 1911, 160.

³⁾ Compt. rend. 152 (1911), 529.

Finally, Group 5 consists of oils which have no effect upon the seedlings. These are oil of cloves, vetiver, and patchouli.

In our last Report we pointed out that the lactone xanthotoxin¹⁾ is a fish-poison. According to H. Priess²⁾, who has thoroughly studied the toxic action of xanthotoxin, this property appears to be common to many lactones. Coumarin, for instance, in aqueous neutral and in faintly acid solution, has considerable activity as an agent for narcotising fish.

J. A. Gardner and W. L. Symes³⁾ have investigated the physiological action of α - and β -camphene phosphonic acid⁴⁾. The examination showed the physiological behaviour of the two acids to be almost identical, both acting more intensely than sodium orthophosphate and less intensely than sodium pyrophosphate. They particularly affect the central nerve-system. They reduce the pressure of the blood, produce excitement when given hypodermically and when given in sufficiently large doses cause death, preceded by unconsciousness. The slowness of the physiological action is due to the fact that camphene phosphonic acids are very rapidly eliminated by the organism.

On the abortive action of oil of *Asarum europæum*, see p. 21.

On the treatment of pulmonary phthisis with oil of cloves, see p. 39.

On a case of poisoning with eucalyptus oil, see p. 49.

On the disinfecting action of menthol, see p. 113.

On the treatment of tuberculous ulcers with niaouli oil, see p. 62.

On a case of poisoning by sassafras oil, see p. 84.

On the pharmacological action of American wormseed oil, see p. 100.

Phyto-physiological Notes.

According to Sack⁵⁾, indole occurs in the perfume of the flowers of *Citrus Aurantium*, L.; *C. decumana*, L.; *C. japonica*; *C. Limonum*, Risso; *C. nobilis*, Lour., and *C. trifoliata*. The presence of the base was shown both by Verschaffelt's⁶⁾ method and by that given by Weehuizen⁷⁾. Indole was

¹⁾ Report April 1911, 73. See the present Report, p. 50.

²⁾ Berichte d. deutsch. pharm. Ges. **21** (1911), 267.

³⁾ Bio-Chemical Journal **5** (1910), 390. From a reprint kindly sent to us.

⁴⁾ Comp. Report April 1894, 70.

⁵⁾ Pharm. Weekblad **48** (1911), No. 13. Quoted from Apotheker Ztg. **26** (1911), 302.

⁶⁾ Comp. Report October 1905, 123.

⁷⁾ Comp. Report April 1909, 140.

also found in the flowers of *Coffea liberica*, *C. robusta*, and *C. Abeokuta*, but only after the flowers had faded. In the case of *Coffea arabica* no reaction could be obtained, notwithstanding the experiment was made with a large quantity of flowers.

The same author has also detected scatole in *Pisi*-wood¹⁾, the presence of the substance being proved by the test with vanillin and hydrochloric acid as well as by Sasaki's²⁾ test with methyl alcohol and sulphuric acid. Hydrocyanic acid and benzaldehyde were obtained from the seed of certain species of *Chrysophyllum*; hydrocyanic acid and acetone from the unripe seed and bark of *Passiflora foetida*, *P. laurifolia*, and *P. quadrangularis*.

According to a subsequent communication by Sack³⁾, indole also occurs in the exhalations (of the flowers?) of *Hevea brasiliensis*, Muell. and of *Randia formosa* (Jacq.), K. Schum.

As stated in our last October Report⁴⁾, Ciamician and Ravenna have demonstrated that salicin is generated from saligenin when the last-named body is brought into contact with the constituents of the living Indian corn plant. The two authors have made subsequent experiments⁵⁾ with a view of determining whether, when benzyl alcohol mixed with glucose is injected into living Indian corn plants, it is capable of forming glucosides. This is probably the case, but it was impossible to isolate any crystalline glucoside-like compound of the alcohol in question.

Sometime ago E. Heckel⁶⁾ observed that anæsthetics possess the power of liberating coumarin from green plants. He⁷⁾ has confirmed this observation with the "Ayapana" (*Eupatorium triplinerve*, Vahl; N. O. Compositæ). This plant is almost odourless in the green state, but when dried it has a characteristic odour of coumarin and of melilotic acid. When, however, the plant is treated with ethyl chloride the odour becomes perceptible after only 5 or 6 minutes, and with ethyl ether or chloroform after about 15 minutes.

Ayapana oil, which has been examined by ourselves⁸⁾ and by Semmler⁹⁾, contained as its principal constituent the dimethyl ether of thymohydroquinone. Coumarin or melilotic acid have not yet been detected in the oil.

¹⁾ In Surinam the name *Pisi* is applied to the wood of *Nectandra* species.

²⁾ Comp. Report October 1910, 203; April 1911, 192.

³⁾ Pharm. Weekblad 48 (1911), 775. Quoted from Chem. Zentralbl. 1911, II. 695.

⁴⁾ Report October 1910, 171.

⁵⁾ Rendiconti della R. Accademia dei Lincei 20, I. (1911), 392. From a reprint kindly sent to us.

⁶⁾ Comp. Report April 1910, 161.

⁷⁾ Compt. rend. 152 (1911), 1825.

⁸⁾ Report April 1907, 106.

⁹⁾ Berl. Berichte 41 (1908), 509; Report April 1908, 17.

As mentioned in our last Report¹⁾, the ultra-violet rays have the power of liberating odoriferous bodies which occur in plants in the form of glucosides. This peculiar property of the ultra-violet rays has recently again been observed by J. Pougnet²⁾ in the case of immature vanilla-pods. It was necessary to expose quite green fruit to the light for about 6 hours, but almost ripe pods only required 20 minutes exposure before the vanilla odour became perceptible.

On the formation and consumption of hydrocyanic acid in the growth of the sweet and the bitter almonds, see under the heading "Almond Oil", p. 17.

Chemical.

For the purpose of completing our previous reference to the 105th paper of Wallach³⁾ on Terpenes and Essential oils, of which we have already made previous mention, based upon the abstract of the paper⁴⁾ which has appeared in the *Nachrichten der K. Ges. d. Wissenschaften zu Göttingen*, October 1910, page 517, we quote the following further details from the original paper: Carvenolide⁵⁾, the lactone obtained when carvone tribromide is reduced by Paal's method, absorbs one molecule hydrogen, with formation of dihydrocarvenolide (m. p. 36 to 38°; b. p. 260 to 261°). This dihydrocarvenolide is most probably identical with pulegenic acid lactone, and, if so, carvenolide would be an unsaturated lactone of pulegenic acid.

Pulegenolide, which was obtained by Wallach⁶⁾ many years ago by acting with sodium hypobromite upon pulegenic acid, was at the time regarded as a saturated compound, owing to the difficulty with which it absorbs halogen. But in the course of the reduction of pulegenolide with hydrogen in the presence of palladium it was found that it does absorb one molecule of hydrogen, and, in the process, yields dihydropulegenolide (m. p. 49 to 50°; b. p. 260 to 261°).

α -Fenchonitrile absorbs 2 atoms of hydrogen, giving rise to dihydro- α -fenchonitrile (b. p. 214 to 215°) a substance which is also obtainable from fencholenic acid amide. For this purpose the latter is reduced by Paal's method, the resulting dihydro- α -fencholenic acid amide (m. p. 133 to 134°) being distilled with phosphorus pentoxide, dihydro- α -fenchonitrile resulting. The reduction of β -fencholenic acid amide proceeds decidedly more slowly than that of the α -amide. Dihydro- β -fencholenic acid amide

¹⁾ Comp. Report April 1911, 160.

²⁾ Compt. rend. 152 (1911), 1184.

³⁾ Liebigs Annalen 381 (1911), 51.

⁴⁾ Report April 1911, 164.

⁵⁾ Liebigs Annalen 305 (1899), 249. Comp. Report April 1899, 56.

⁶⁾ Liebigs Annalen 300 (1898); Report October 1898, 52.

(m. p. 94°), is identical with fencholic acid amide¹⁾. When heated with hydrochloric acid in a sealed tube the amide yielded dihydro- β -fencholenic acid, which is identical with fencholic acid. Dihydro- α -fencholenic acid boils at 259 to 260° .

Dihydrothujaketone, to which a brief reference was made in our previous Report²⁾, boils between 183 and 185° . When reduced with sodium in alcoholic solution it yields dihydrothujaketol (b. p. $191,5$ to $192,5^{\circ}$). When treated with methyl magnesium iodide, dihydrothujaketone yields a tertiary alcohol with an agreeable rose-like odour, b. p. 192 to 194° .

The reduction of tanacetophorone gave rise to isopropyl-1-cyclopentanone-3.

The reaction of hexahydro- p -acetyloluene³⁾ with methyl magnesium iodide yielded p -menthanol-8 (b. p. 209 to $211,5^{\circ}$; $d_{19^{\circ}}$ $0,9090$; $n_{D16^{\circ}}$ $1,4640$).

Hydrocarbons.

Isoprene. According to H. Staudinger and H. W. Klever¹⁾, a substantial yield of isoprene, an olefinic hydrocarbon which occurs as a decomposition-product of turpentine oil and caoutchouc, may be obtained by heating dipentene- or limonene-vapour in the rarified state at high temperatures. The rarification may be attained either by evacuation or by mixing with indifferent gases. The heating is best done by means of glowing metallic wire. Yields up to 60% have been obtained by this method. The vapour of turpentine oil yields but little isoprene; terpinolene and terpinene are not easy to decompose. Camphene and pinene yield none, or only a small proportion of isoprene.

For the purpose of decomposing certain terpene-bodies, in particular limonene, by means of red-hot metal wires, Harries and Gottlob²⁾ have constructed what they term an isoprene-lamp. This apparatus consists of a flask or bulb in which is placed a platinum wire 120 cm. long which, at an average red-hot temperature, has a resistance of 9Ω , and requires about 5 amperes at 220 volts. The flask is connected with a vertical condenser at the top of which is a delivery-tube for the isoprene-vapour. The non-decomposed terpene drops down the condenser and the isoprene is collected in a receiver which has been cooled down by a freezing mixture. Pinene only gave about 1% of isoprene, but commercial carvene, according to its limonene-content, yielded up to nearly 50% of almost pure isoprene.

1) Comp. Report April 1911, 185.

2) *Ibidem* 165.

3) *Ibidem* 165.

4) Berl. Berichte 44 (1911), 2212.

5) Liebigs Annalen 383 (1911), 228.

Isoprene, which is regarded as the fundamental substance of the terpenes, is well-known to play a leading part in the manufacture of artificial rubber. It can be prepared synthetically by various processes. According to Harries¹⁾, pure isoprene is obtainable from β -methyltetramethylene glycol $\text{H}_3\text{C} \cdot \text{CH} \cdot \text{CH}_2\text{OH}$, which is prepared by heating pyro-

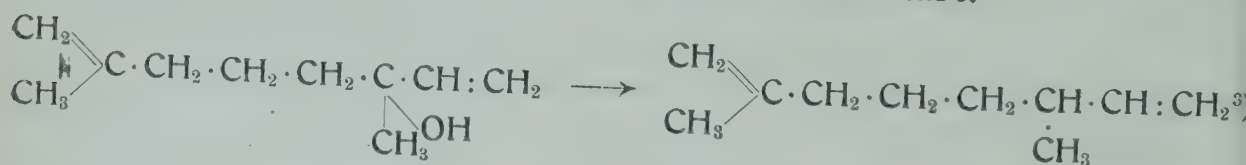


tartaric acid diethylate with sodium. When the glycol is heated with hydrobromic acid of 60% in a sealed tube to 100°, β -methyltetramethylene bromide is generated, and this, when heated with trimethylamine in fused glass-tubes to 100°, yields an isoprene possessing the following constants: b. p. 36 to 37°, d_{210} 0,6804, n_{D210} 1,42267.

We cannot spare the space here to describe in detail the synthesis of isoprene into rubber. It is polymerised into rubber, or into a substance closely resembling natural rubber, by merely heating it for a longer or shorter period, according to the temperature applied, in a closed vessel.

It is extremely difficult to differentiate between artificial and natural rubber: only two compounds can be used for this purpose, *viz.*, the nitrosite and the tetrabromide, both of which are amorphous, have no definite m. p. and either cannot be purified at all, or only with difficulty.

Linaloolene. Apart from recent work by means of metals acting as catalysers, Semmler is the only investigator who has carried out experiments in reduction of the aliphatic terpene-alcohol series. Semmler²⁾ has ascertained that geraniol, in contradistinction to linalool, is very stable against nascent hydrogen derived from chemical sources, whereas linalool yields a hydrocarbon, linaloolene, in the generation of which the hydroxyl-group is replaced by hydrogen ("elimination of the oxygen"). The abstraction of oxygen may be accomplished, in the case of linalool, either by reduction with sodium in a solution of ethyl or amyl alcohol or in excess of linalool, or by heating the linalool with zinc-dust in a sealed tube.



In Semmler's opinion⁴⁾, linaloolene is only an isomeride of dihydromyrcene, the reduction-product of the aliphatic terpene hydrocarbons myrcene and

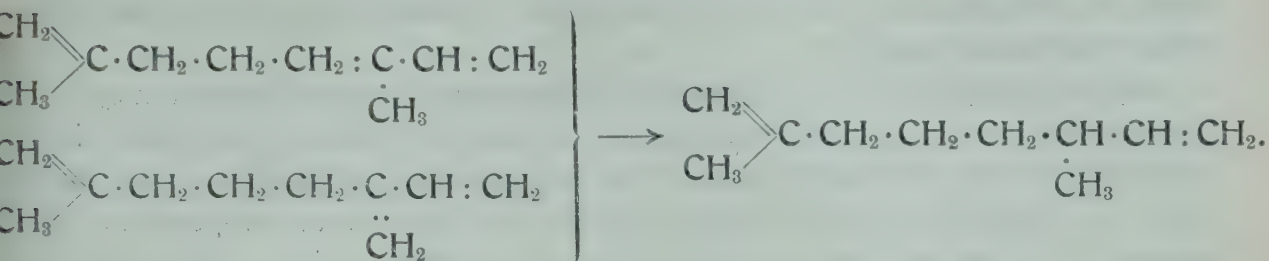
¹⁾ Liebigs Annalen 383 (1911), 157.

²⁾ Berl. Berichte 27 (1894), 2520.

³⁾ All the schemes of molecular structure are set out in the limonene formula; but it would of course be equally proper to adopt the terpinolene formula favoured by Enklaar. It is evident that oxidative resolution alone could supply definite proof whether only one of two formulæ or a mixture of both is present.

⁴⁾ Berl. Berichte 34 (1901), 3122.

ocimene, "although the physical data of linaloolene agree almost completely with those of dihydromyrcene".



By reacting with sodium upon linalool we obtained as a by-product a small yield of a hydrocarbon with the following constants: b. p. 169 to 170°, d_{150} 0,7900, $\alpha_D - 0^\circ 43'$, n_{D150} 1,45341, n_{D200} 1,45191. After fractionation over sodium the principal portion (95%) boiled at 58° (12 mm.), giving d_{150} 0,7824; n_{D150} 1,45251; mol. refr. found 47,60, calc. as $\text{C}_{10}\text{H}_{18/2}$ 47,32.

This linaloolene prepared by us absorbed 4 atoms of bromine, with formation of a readily-crystallising tetrabromide, m. p. 88 to 88,5°, which proved to be identical with dihydromyrcene tetrabromide, a body first prepared by Enklaar¹⁾. It follows from the above that linaloolene and dihydromyrcene are identical.

The constants of the products obtained by each of the various investigators are given below for purposes of comparison:

	Linaloolene (Semmler)	Dihydromyrcene	Dihydromyrcene	Dihydro ocimene	Dihydromyrcene (Schimmel & C ²)
			(Enklaar)		
B. p.	165 to 168 °	171,5 to 173,5 °	166 to 168 °	166 to 168 °	168 °
Sp. gr.	0,7882 (20 °)	0,7802 (? °)	0,7852 (15 °)	0,7750 (15 °)	0,7824 (15 °)
Refr.	1,455 (20 °)	1,4501	1,4514 (17 °)	1,4507 (17 °)	1,45251 (15 °)
Mol. Refr. found	—	—	—	47,62	47,60
Mol. Refr. calc. as $\text{C}_{10}\text{H}_{18/2}$	—	—	—	47,34	47,32

The preparation of dihydromyrcene tetrabromide is often attended by difficulties. The method recommended by Enklaar, and recently also adopted by Semmler²⁾, of dissolving the hydrocarbon in glacial acetic acid, has not stood the test of practice, because it generally gives rise to oily bromides. Hydrobromic acid appears to be evolved as soon as the bromine is added to the glacial acetic acid solution. The reaction is accomplished more quickly and effectively by dissolving the hydrocarbon in a mixture of one part by volume of amyl alcohol and two parts by

¹⁾ Over Ocimeen en Myrceen, eene bijdrage tot de kennis van de aliphatische terpenen. Inaug. Dissert. Utrecht 1905. p. 34. Report April 1906, 109.

²⁾ Berl. Berichte 44 (1911), 2011.

volume of ether. Shortly after the addition of the calculated quantity of bromine (a possible excess of bromine may be removed by adding a few drops of the hydrocarbon) the tetrabromide separates out in the form of a solid crystalline paste.

By inverting linaloolene and dihydromyrcene Semmler obtained *cyclo*-linaloolene and *cyclodihydromyrcene*. Linaloolene being identical with dihydromyrcene, the same applies to the products of inversion. In the case of dihydromyrcene Semmler carried out the inversion-process by means of a mixture of glacial acetic and sulphuric acids. With regard to this process he remarks¹⁾: "this inversion is most easily carried out with glacial acetic acid and sulphuric acid, where, theoretically, an alcohol should be expected".

Working at a low temperature it is not particularly difficult to isolate the alcohol in question. From 200 g. dihydromyrcene we obtained from 120 to 130 g. *cyclodihydromyrcene* and between 64 and 67 g. ester; the latter boiling between 97 and 103° (12 mm.). The constants of the two ester-fractions were as follow:

- | | |
|---|--|
| I. d_{150} 0,8780, n_{D150} 1,44741, ester v. 271, mol. refr. found 60,61 | } $C_{12}H_{22}O_2$ $\sqrt{\frac{2}{3}}$ 59,67. calc. as |
| II. d_{150} 0,8857, n_{D150} 1,44549, ester v. 279, mol. refr. found 58,8 | |

The alcohol obtained by saponification gave:

I. Fract.	} B. p. 92 to 92,5° (12 to 13 mm.) or 200° at atmosph. pressure.	d_{150} 0,8563, n_{D150} 1,45591, mol. refr. found 49,54,	} calc. a $C_{10}H_{20}O$ 49,438
II. Fract.		d_{150} 0,8557, n_{D150} 1,45471, " " 49,48,	
III. Fract.		d_{150} 0,8564, n_{D150} 1,45641, " " 49,50,	
IV. Fract.		d_{150} 0,8570, n_{D150} 1,45531, " " 49,47,	

0,1456 g. subst.: 0,4099 g. CO₂, 0,1556 g. H₂O.

	Found	Calc. as $C_{10}H_{20}O$
C	76,81%	76,92%
H	13,06%	12,82%

When gently heated with formic acid the alcohol gave off water; towards oxidation with chromic acid in glacial acetic acid and bichromate in dilute sulphuric acid it was very stable, and the reaction did not give rise to any ketone or aldehyde. With phenylisocyanate it yielded a phenylurethane (m. p. 61°) which crystallised out in fine needles.

Oxidation with a 1/2% solution of permanganate of potassium yielded as the principal product of reaction a glycerol, b. p. 165 to 170° (7 mm.), together with a lactone and succinic acid.

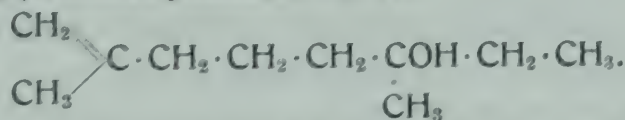
0,1299 g. subst.: 0,2995 g. CO₂, 0,1269 g. H₂O.

	Found	Calc. as $C_{10}H_{22}O_3$
C	62,87%	63,13%
H	11,94%	11,57%

¹⁾ Berl. Berichte 34 (1901), 3128.

Further oxidation of the glycerol with bichromate and sulphuric acid yields succinic acid, m. p. 183 to 185°, together with a lactone, m. p. 210 to 220°, which, when treated with nitric acid, is likewise converted into succinic acid; but neither lævulic acid nor methylheptenone is formed. When the glycerol is carefully oxidised with a quantity of bichromate calculated for 1 atom oxygen, it is also possible to isolate the dihydroxy aldehyde, which very readily reduces ammoniacal silver solution.

All the data enumerated above indicate that the alcohol which is formed by hydrating dihydromyrcene must possess the constitution of dihydrolinalool (2,6-dimethyloctene-1-ol-6).



For purposes of comparison we have prepared the alcohol according to Enklaar's method¹⁾, by reacting with magnesium iodoethyl upon methylheptenone (obtained by oxidising citral):—

B. p. 77 to 78° (7 mm.) or 83 to 84° (9 mm.); $d_{15} 0,8588$; $n_{D15} 1,45641$; $n_{D20} 1,45471$; $\alpha_D + 0$; mol. refr. found 49,46, calc. as $\text{C}_{10}\text{H}_{20}\text{O}/1$ 49,438.

Enklaar gives the following constants: $d_{15} 0,8695$, $n_{D15} 1,4569$. It may be questioned, however, whether these values are correct, for by all experience it appears to be impossible that the disappearance of an ethylene-bond should not be attended by a concurrent decrease of sp. gr. (e. g., geraniol-citronellol, carvone-dihydrocarvone-tetrahydrocarvone, &c.).

The phenylurethane of dihydrolinalool prepared from methylheptenone does not form so readily as that of dihydrolinalool prepared by the hydration-method. It was most difficult to obtain it in the pure state and it appears to consist of a mixture of the two isomerides (the limonene- and the terpinolene-modification).

The alcohol prepared from methylheptenone (from lemongrass oil) and from magnesium ethyl iodide also yielded no uniform phenylurethane. The constants of this alcohol resembled those of the alcohol obtained from the synthetic methylheptenone, b. p. 66 to 66,5° (4 mm.), $d_{15} 0,8575$, $\alpha_D \pm 0$, $n_{D20} 1,45391$, mol. refr. found 49,558, calc. for $\text{C}_{10}\text{H}_{20}\text{O}/1$ 49,438.

Cyclodihydromyrcene, the body which, together with the alcohol, was formed in the process of hydration, boiled between 167 and 169°; $d_{15} 0,8328$; $n_{D15} 1,46288$; mol. refr. found 45,63, calc. as $\text{C}_{10}\text{H}_{18}/1$ 45,61.

	Cyclodihydromyrcene (Schimmel & Co.)	Cyclodihydromyrcene (Semmler)	Cyclolinaloolene
B. p.	167 to 169°	169 to 172°	165 to 167°
Sp. gr.	0,8328 (15°)	0,828 (20°)	—
Refraction	1,46288 (15°)	1,462	—
Mol. refr.	45,63	45,63	—

¹⁾ Recueil trav. chim. des P.-B. 27 (1908), 411. Comp. Report April 1909, 125.

The hydrocarbon absorbs 2 bromine-atoms; neither a nitrosochloride nor a nitrosate being formed, although according to the molecular structure as given by Semmler the formation of such bodies was to be expected. When oxidised with permanganate the principal reaction-product is the ketonic acid, as already discovered by Semmler. In this reaction a portion of hydrocarbon remains remarkably stable (b. p. 171 to 172°; d_{150} 0,8363 to 0,8406) from which it may perhaps be inferred that *cyclodihydromyrcene* is a mixture of isomeric hydrocarbons. From 1 kilo *cyclodihydromyrcene* we obtained 200 grms. ketonic acid, b. p. 141 to 142° (6 mm.); a small quantity dicarboxylic acid, and a volatile body: b. p. 224°, m. p. 17 to 18°; 550 grms. of the hydrocarbon remained unattacked. We intend to report further on the progress of this investigation, the object of which is to determine the constitution of the hydrocarbon in question.

F. Taboury and F. Bodroux¹⁾, in the course of a repetition of the bromination of *cyclohexane*, *methylcyclohexane* and *dimethylcyclohexane* carried out by Kishner²⁾ and Markownikow³⁾, have obtained results differing altogether from those of the Russian chemists. Their attempt to brominate menthene and thymomenthene was also a failure. The reaction-product formed a syrupy mass, from which no characteristic product could possibly be obtained.

Bicyclohexene. Detailed particulars on the preparation of *bicyclohexene*⁴⁾ are to be found in Wallach's 106th paper on Terpenes and Essential Oils⁵⁾.

Camphene. The question of the uniformity of camphene is of great importance in considering the constitution of this hydrocarbon. Aschan⁶⁾ has attempted to solve the problem by preparing crystalline derivatives of the body, but no comparison of camphene hydrochloride with the chlorides of borneol and *isoborneol* was possible, because it was not certain that the last-named bodies are capable of being recrystallised without molecular rearrangement. Hence the only feasible conversions are those which can be carried out with agents in which atomic transposition is out of the question. Such a reagent is milk of lime. Some years ago Aschan⁷⁾ had observed that when milk of lime is allowed to act upon camphene hydrochloride, an alcohol results to which he gave the name

¹⁾ Bull. Soc. chim. IV. 9 (1911), 595.

²⁾ Journ. russ. phys. chem. Ges. 23 (1891), 20.

³⁾ *Ibidem* 30 (1898), 151.

⁴⁾ Comp. Report April 1911, 167.

⁵⁾ Liebigs Annalen 381 (1911), 112.

⁶⁾ Liebigs Annalen 383 (1911), 1.

⁷⁾ Comp. Report November 1908, 179.

of camphene hydrate. In like manner as camphene hydrochloride, bornyl- and *isobornyl* chlorides react with milk of lime. But, whereas bornyl chloride gives an almost quantitative yield of camphene hydrate, *isobornyl* chloride yields hardly anything except camphene and a very little camphene hydrate. The behaviour of camphene hydrochloride being midway between that of the two other bodies, Aschan assumes the last-named to represent a mixture of two hydrochlorides, α - und β -camphene hydrochloride, of which the α -modification, when treated with weak alkalies, yields camphene hydrate, while the β -modification yields camphene. Assuming this view to be correct, bornyl chloride would consist chiefly of α -, and *isobornyl* chloride chiefly of β -camphene hydrochloride. Both α - and β -camphene hydrochloride behave after the manner of tertiary terpene hydrochlorides, for which reason they cannot be direct derivatives of the two secondary alcohols borneol and *isoborneol*. Aschan was able to prove that both hydrochlorides are derived from the same camphene. In order to establish this, he converted terecamphene (prepared from the hydrochloride of American turpentine oil by heating with bases) into its hydrochloride and recovered camphene hydrate from the latter. When treated with glacial acetic acid this camphene hydrate yielded camphene, which again produced the original hydrochloride of the same rotation. It would therefore appear that the conversion of camphene into the hydrochloride and into camphene hydrate and *vice versa*, is accomplished without transposition of the carbon-skeleton. The camphene produced from β -camphene hydrochloride also gave almost the same rotation as did the fundamental substance, and it is therefore very probable that the fundamental substance was a uniform body. The same results were observed with a camphene of high rotatory power from Siberian pine needle oil.

Aschan has not succeeded in separating α - and β -camphene hydrochloride. Occasionally, but not always, it was possible to purify the α -derivative by recrystallising it from light petroleum (m. p. 150 to 151°; the highly-active modification melts at 157 to 158°). The behaviour of the crude hydrochlorides towards seminormal alkali-liquor at 50° enabled a quantitative estimate of the constituents to be made. From time to time samples were drawn from the solutions in order to control the consumption of potash liquor according to the equation $C_{10}H_{17}Cl + KOH = C_{10}H_{16} + KCl + H_2O$. The examination showed the camphene hydrochloride content of the crude *isobornyl* chloride to be from 60 to 70%. Pinene hydrochloride, after frequent recrystallisation, also contains about 10% of a readily-decomposing hydrochloride which may perhaps consist of a mixture of α - and β -camphene hydrochloride. Unfortunately, considerations of space prevent us from going into the experimental details of this interesting investigation, for which we must refer to the original paper.

In his third paper on the constitution of camphene, Aschan¹⁾ discusses the experiments in oxidation which he has carried out with this hydrocarbon. Camphenes of different origin, (technical c., c. from *iso*-borneol, c. from *l*-borneol, Kahlbaum's c., c. from Siberian pine needle oil, recrystallised technical c., and c. from Greek turpentine oil) gave the same oxidation-products in constant quantitative proportions. The principal product formed was camphenic acid, in addition to which camphenilone, camphenyl glycol, camphenilic acid and acids soluble in water were generated. For purposes of oxidation, 25 g. camphene was dissolved in 5 g. benzene and diluted with a solution of $\frac{1}{2}$ liter water and 7,5 g. caustic potash. This mixture was slowly oxidised at ordinary temperature with the oxidation-liquid, which consisted of 64 g. permanganate of potassium in 3,2 liters water.

The results of his experiments in oxidation lead Aschan to the following conclusion: "camphene represents an ethylenic complex with the double-bond in the ring, or it is of a tricyclic structure, perhaps with one trimethylene-ring, which opens very readily, producing an ethylenic complex of the above character".

Aschan's fourth paper²⁾ deals with of the stereomeric camphenic acids. *cis*-Camphenic acid (m. p. 135,5 to 136,5°), obtained by oxidising technical camphene, m. p. 42°, was heated in a sealed tube with a mixture of glacial acetic and hydrochloric acids to 180°. From the reaction-product the author isolated, in addition to unattacked acid, a *d,l-trans*-camphenic acid (m. p. 122 to 123°) from which he obtained a diamide, m. p. 231 to 232°, and a dianilide, m. p. 165°. He also reduced *cis-α*-bromocamphenic acid with zinc and glacial acetic-hydrochloric acid, the result being almost equal quantities of *cis*- and *trans*-camphenic acid. Distillation of the *cis*-camphenic acid under diminished pressure also resulted in the partial conversion of the *cis*- into the *trans*-acid. When distilled under ordinary pressure, *cis*-camphenic acid is decomposed, an acid $C_9H_{14}O_2$ being formed.

When camphene is oxidised with hydrogen peroxide changes in its molecular structure are hardly to be expected, hence the results obtained by G. G. Henderson and M. M. J. Sutherland³⁾ when oxidising camphene with the reagent in question are of particular interest. The principal reaction-product was a monobasic acid of the formula $C_9H_{15}CO_2H$ (m. p. 95°), to which the name camphylic acid was given; in addition a solid acid (m. p. about 70°) and a liquid acid, b. p. 153° (20 mm.) were formed. The constitution of camphylic acid could not be determined, but it appears that its nucleus is different from that of camphene. Of neutral oxidation products,

1) Liebig's Annalen 383 (1911), 39.

2) *Ibidem* 52.

3) Journ. chem. Soc. 99 (1911), 1539.

camphenilone was found, also *isocamphenilanaldehyde* and a compound (b. p. 94 to 96° at 14 mm.) of the formula $C_9H_{16}O_2$; the last-named, when treated with phthalic anhydride, yielded an alcohol $C_9H_{16}O$. In addition to the above, small quantities of camphene glycol and a neutral body, m. p. 69°, were observed as oxidation-products. Camphylic acid dissolves with exceptional ease in the usual organic solvents; it yields a chloride (b. p. 110° at 17 mm.) which, when treated with bromine, gives rise to the chloride of bromocamphylic acid. Bromocamphylic acid melts at 210°, and when heated with aqueous soda-solution is converted into hydroxycamphylic acid, m. p. 245°. The oxidation of camphene was accomplished by heating 1 mol. of the hydrocarbon with 3 mols. hydrogen peroxide (in 30% solution) and 4 times its weight of glacial acetic acid in a reflux condenser to about 60°. Several days were required to complete the reaction, its termination being indicated by the fact that no further camphene was deposited in the condenser.

Several years ago, while oxidising camphene for the purpose of preparing apocamphoric acid, Komppa obtained as a by-product an acid which he has recently investigated more closely¹⁾ and found to be identical with ketopinic acid. This acid melts at 233,5 to 234,5° and yields a phenylhydrazone melting at 146°. Its combustion is very difficult to accomplish, good results being only obtained with a chromate-of-lead-asbestos tube.

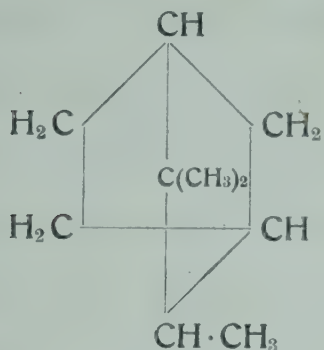
For the purpose of preparing *isocamphane* P. Lipp²⁾ has reduced camphene ($[\alpha]_{D220} - 18,94^\circ$) from pinene hydrochloride according to the method of Sabatier and Senderens. In the course of his proceedings he obtained two isomerides, a liquid *isocamphane* (b. p. 160 to 162°; $d_{40}^{20} 0,8524$; $[\alpha]_{D190} + 1^\circ 15'$; $n_{D20} 1,45733$) as well as a solid modification with m. p. 65 to 67°. The last-named compound is obtained in an almost quantitative yield from camphene from *isoborneol*. The author also prepared solid *isocamphane* by reducing *i*-camphane by Fokin's³⁾ method with platinum black and hydrogen. Finally he obtained from *l*-camphene ($[\alpha]_{D190} - 80,7^\circ$) a solid *d*-*isocamphane*: $[\alpha]_{D220} + 8,68^\circ$. Oxidation with permanganate of potassium in a solution of acetic acid gave rise to a mixture of stereoisomeric camphenilanic and *isocamphenilanic* acid, which proves that camphene and *isocamphane* still possess the same carbon skeleton. This fact was further confirmed by oxidising with nitric acid, for in the course of this reaction the same oxidation-products were formed as in the oxidation of camphene. The acid oxidation-products consist principally of carbonylapocamphoric acid. The formation of this acid shows that a rear-

¹⁾ Berl. Berichte **44** (1911), 863.

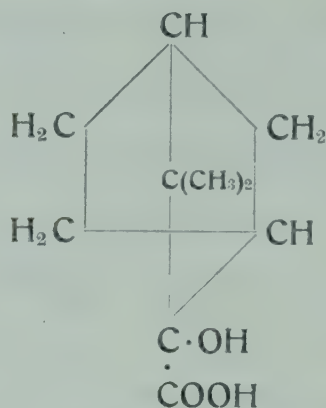
²⁾ Liebigs Annalen **382** (1911), 265.

³⁾ Zeitschr. f. angew. Chem. **22** (1909), 1496; Zeitschr. f. anal. Chem. **48** (1909), 337.

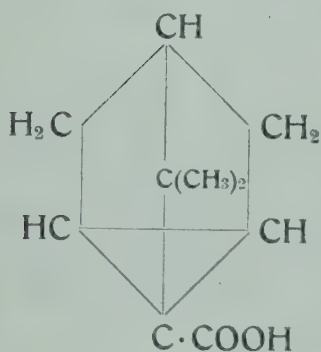
rangement must take place of the camphene-type into the camphor-type; possibly on the lines set forth below:



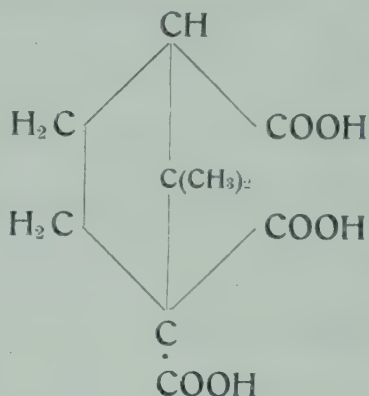
Isocamphane.



Camphenylic acid.



Tricyclene carboxylic acid.



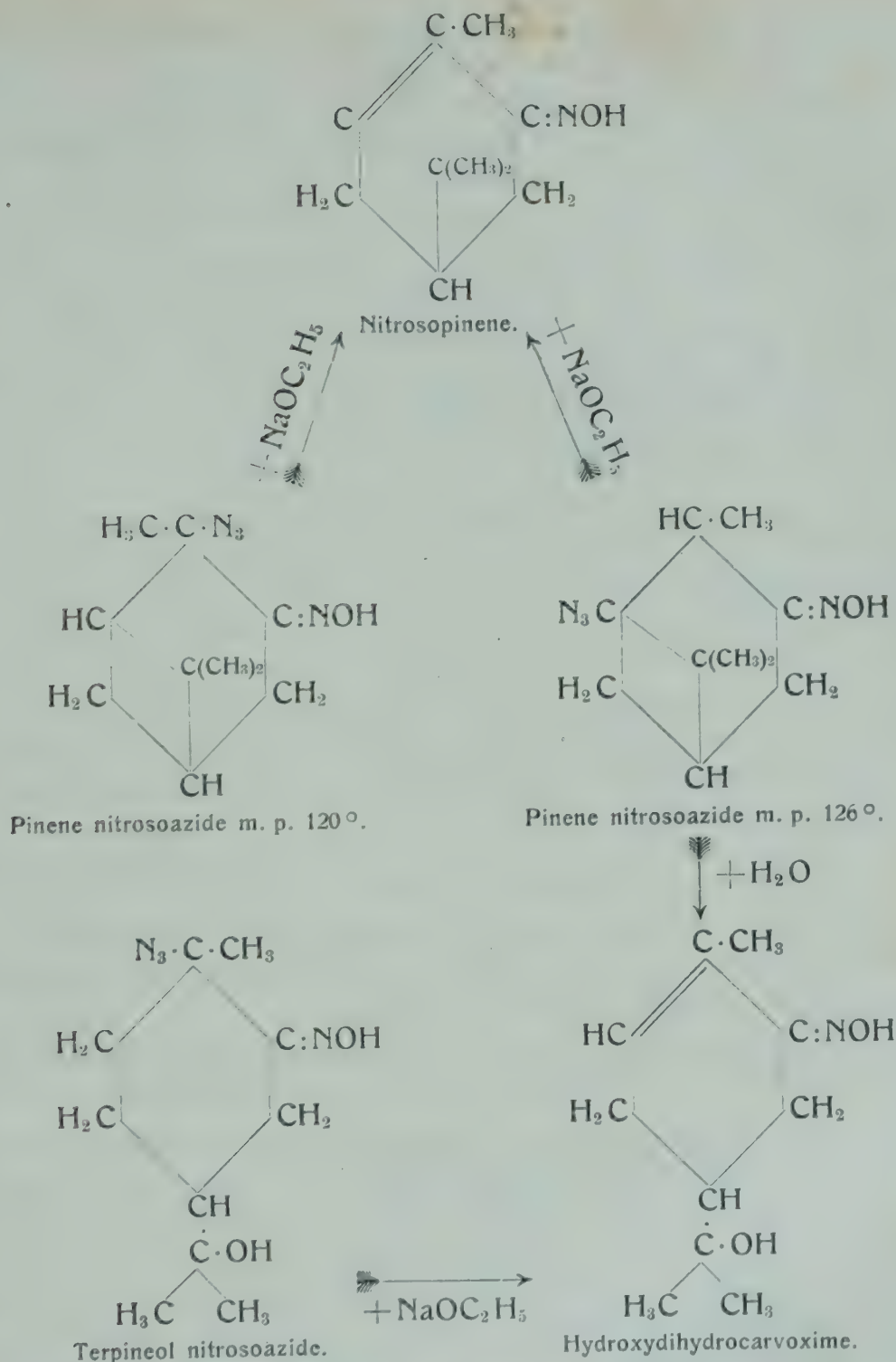
Carboxyl apocamphoric acid.

Lipp is of opinion that these experiments prove the uniformity of camphene from *isoborneol*.

On the formation of *isobornyl* formate from camphene see p. 142.

α -Pinene. M. O. Forster and S. H. Newman¹⁾ have discovered that when an alcoholic solution of pinene nitrosochloride is heated with sodium azide, pinene nitrosoazide is formed. This substance appears in the form of brilliant, colourless, transparent prisms, m. p. 120°. When this compound is treated with acetic anhydride there results the acetyl derivative (m. p. 64°); treatment with sodium alcoholate yields nitrosopinene. A modification melting at 126° is obtained by heating the pinene nitrosoazide with water and alcohol. This isomeride also, when treated with sodium alcoholate yields nitrisopinene; its acetyl compound melts at 71°. When the pinene nitrosoazide melting at 126° is heated with water it yields hydroxydihydrocarboxime, which substance was also obtained from terpineol nitrosoazide, m. p. 111° (a body also prepared by the authors) by treating it with sodium alcoholate. The molecular structure of these bodies is shown below: —

¹⁾ Journ. chem. Soc. 99 (1911), 244.



The paper by Vavon on the hydrogenation of turpentine oil to which reference was made in our last October Report (p. 166) has now been published in another periodical¹⁾.

Limonene. Some time ago we reported that Vavon²⁾ had reduced limonene by shaking it with platinum black in an atmosphere of hydrogen.

¹⁾ Bull. Soc. chim. IV. 9 (1911), 256.

²⁾ Comp. Report April 1910, 166.

Since then the same author has continued his investigations¹⁾ and has discovered that the hydrogenation of limonene takes place in two phases. In the first stadium a hydrocarbon $C_{10}H_{18}$ is formed, and this body yields the ultimate product $C_{10}H_{20}$. The last-named compound being inactive, examination of the rotation shows how far the process of reduction has proceeded. By this means it was easy to obtain the hydrocarbon $C_{10}H_{18}$ in the pure state. Its constants are as follow: b. p. 175 to 177°, $d_{15} 0,8246$, $[\alpha]_{578} + 118^\circ$, $n_{D180} 1,4563$. The dibromo derivative possessed the following properties: b. p. 136 to 140° (16 mm.), $d_{40}^{210} 1,459$, $[\alpha]_{578} + 49^\circ$, $n_{D210} 1,5236$. The nitrosochloride ($[\alpha]_{578} + 344^\circ$) melts between 95 and 96°.

This dihydrolimonene is probably pure *d*-carvomenthene, while the product obtained by Wallach²⁾ was partly racemised.

Dipentene. By treating dipentene nitrosochloride or nitrosate with sodium azide, M. O. Forster and F. M. van Gelderen³⁾ have succeeded in preparing dipentene nitrosoazide, $C_{10}H_{15}(:NOH)N_3$, a compound with m. p. between 72 and 73°, and consisting of colourless plates. With alcoholic potash liquor hydrazoic acid is eliminated from the azide, *i*-carvoxime being produced. Reaction of hot aqueous oxalic acid with the nitrosoazide yields *d,l*-triazodihydrocarvone, $C_{10}H_{15}ON_3$, a colourless liquid with an agreeable odour reminding of peppermint: b. p. 81° (0,4 mm.), $d_{200} 1,0409$. The semicarbazone melts at 132 to 133°.

The corresponding derivatives of *d*- and *l*-limonene were obtained by the same method. *d*- and *l*-limonene nitrosoazide melt between 52 and 53°: $[\alpha]_D + 6,5^\circ$ and -3° respectively. Treatment of the azides with alcoholic potash liquor gives rise to *l*- and *d*-carvoxime respectively. *d*- or *l*-triazodihydrocarvone has the following constants: b. p. 93° (0,46 mm.) and 93 to 94° (0,48 mm.) respectively; $d_{200} 1,0487$ and $1,0472$ respectively and $[\alpha]_D + 88,49^\circ$ and $-92,5^\circ$ respectively. Both semicarbazones melt at 220°.

According to A. H. Richard⁴⁾, the polymerisation of dimethylbutadiene gives rise to a rubber-like mass from which by means of dry distillation a yield of about 50% of a homologue of terpene, probably dimethyl-dipentene, $C_{12}H_{20}$, may be obtained. This hydrocarbon possesses the following constants: b. p. 97 to 98° (22 mm.), about 205° at ordinary pressure, $d_{00} 0,872$, $d_{40}^{250} 0,85322$, $\alpha + 0$, $n_{D250} 1,47786$. Reduction with platinum black and hydrogen results in a hydrocarbon $C_{12}H_{22}$, possessing the following constants: b. p. 93 to 95° (20 mm.), $d_{00} 0,860$, $d_{40}^{250} 0,842307$, $n_{D250} 1,46635$. No crystalline tetrabromide or hydrochloride of dimethyl-dipentene was obtained, but the author obtained a small yield of the hydrochloride of a nitrosochloride (m. p. about 160°).

¹⁾ Compt. rend. 152 (1911), 1675.

²⁾ Liebigs Annalen 277 (1893), 132.

³⁾ Proceed. chem. Soc. 27 (1911), 195.

⁴⁾ Compt. rend. 153 (1911), 116.

Alcohols.

We have already previously referred to the glucosides of menthol and borneol prepared by E. Fischer und K. Raske¹⁾. Since then, E. Fischer and B. Helferich²⁾ have described the glucosides of cetylalcohol, geraniol, cyclohexanol, benzylalcohol and glycolic acid. β -Geraniol-*d*-glucoside was prepared by shaking up geraniol with aceto-bromoglucose in ether with oxide of silver. When the excess of geraniol had been blown off with steam, an oil remained behind from which, after prolonged standing, tetracetyl- β -geraniol-*d*-glucoside crystallised out. This body melts at 29 to 30°. After saponification with barium hydroxide, the β -geraniol-*d*-glucoside was obtained from the acetylated compound. Dried over phosphorus pentoxide this glucoside gave $[\alpha]_{D27^\circ} - 37,25^\circ$. It is tolerably hygroscopic, has an exceedingly bitter taste, and melts at 58°. When the aqueous solution is evaporated the geraniol glucoside is left behind in the form of beautiful hydrated needles, $C_{16}H_{28}O_6 \cdot \frac{1}{2}H_2O$. The glucoside dissolves very readily in alcohol and water, less readily in acetone and acetic ester, and is very little soluble in ether and light petroleum.

Tetracetyl- β -benzyl-*d*-glucoside, which is prepared in a similar manner, melts, not very definitely, between 96 and 101°; β -benzyl-*d*-glucoside melts at 123 to 125°. Tetracetyl- β -cyclohexanol-*d*-glucoside occurs in long needles with a silky lustre, m. p. 120 to 121°. β -Cyclohexanol-*d*-glucoside melts between 133 and 137°.

By condensing the hydrobromic ester of geraniol (or of linalool)³⁾ with malonic ester or acetic ester, Dupont and Labaune⁴⁾ have prepared certain new derivatives of geraniol or linalool, as the case may be.

To the alcoholic solution of sodium malonic ester they added the bromide by degrees, the temperature being meanwhile kept at about 10°, as otherwise geranyl ethyl ether would have been formed. The principal product obtained was a substituted malonic diethylester, answering to formula I, which upon saponification yielded an acid (II) from which on distillation *in vacuo* one molecule carbon dioxide was split off, with formation of a substituted acetic acid (III) (b. p. 145 to 146° at 5 mm.; b. p. of the ethyl ester 127 to 128° at 5 mm.). It was impossible to convert the ester into a cyclic derivative by treating it with acids, even sulphuric acid of 66° B was without effect in the cold. In the course of the reduction of the ester of the substituted acetic acid with sodium and alcohol, an alcohol (IV) was obtained which, when regenerated from the phthalic ester, was found to possess the following constants: b. p. 119° (5 mm.), $d_{18^\circ} 0,8956$,

¹⁾ Berl. Berichte **42** (1909), 1465. Comp. Report October **1909**, 78.

²⁾ Liebigs Annalen **383** (1911), 68.

³⁾ Comp. Report April **1910**, 172; October **1910**, 188.

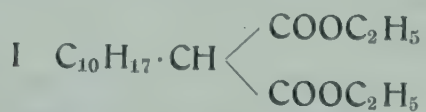
⁴⁾ Berichte von Roure-Bertrand Fils, April **1911**, 3.

n_{D180} 1,4755. No hydrogen had been added to the linalyl radical. The pyruvic ester of the new alcohol boiled at 135° (6 mm.) and yielded a semicarbazone melting at 103° . An attempt to prepare the aldehyde corresponding to the alcohol was unsuccessful.

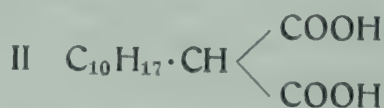
The odour of all the bodies mentioned above was much weaker than that of linalool or geraniol, hence the enlarging of the molecule of these alcohols is attended by a diminution in the degree of intensity of the odour.

When the hydrobromic ester was condensed with sodium acetate, the result was a ketonic ester, for which structure V may be assumed. When saponified with alcoholic potash liquor the ketonic ester gave off carbonic acid, a ketone (VI) being formed. The hydrazone of this ketone boiled at 125° (6 mm.); the semicarbazone had m. p. 86° .

When the ketone is oxidised with permanganate of potassium and chromic acid it most probably yields levulic acid; before the structure of the group $C_{10}H_{17}$ can be discussed it is necessary to await the result of further investigations.



Substituted malonic dimethylester.



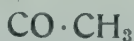
Acid.



Substituted acetic acid.



Alcohol.



Ketonic ester.



Ketone.

On β -geraniol-*d*-glucoside see p. 139.

On isogeraniol see p. 145.

Linalool. We have lately noticed that the specific gravity of linalool prepared by us from essential oils was frequently lower than we had for a long time been used to observe, either in the commercial article, or in linalool isolated from various kinds of essential oils. A sample of such a linalool, which has been examined by us, gave the following constants: b. p. 199 to 200° , d_{150} 0,8664, $\alpha_D - 17^{\circ} 30'$, n_{D200} 1,46288, mol. refr. found 49,17, calc. as $C_{10}H_{18}O_{\frac{1}{2}}$ 48,97. Estimation of the linalool by 6 hours boiling with acetic anhydride¹⁾ in xylene solution gave an alcohol-content of 93%; in toluene solution the alcohol absorbed the calculated quantity of sodium without any solid matter being separated from it.

In spite of repeated careful fractionation we were unable to observe any greater variations in density, rotatory power or refractive index; hence

¹⁾ Report April 1907, 120.

the accumulation of a possibly-present foreign body as a result of distillation was out of the question. We then attempted, by oxidising with chromic acid and bichromate of potassium, and by using phthalic anhydride, formic acid, glacial acetic and sulphuric acids and semicarbazide, to isolate or accumulate a substance of some sort which would enable us to infer the presence of a foreign body in addition to linalool, but again without success. Finally we made the experiment of preparing a pure linalool by splitting up linalylphenylurethane, a substance which can be prepared without difficulty in the pure state. We caused 50 grms. of our linalool to react with 40 grms. phenylisocyanate. The resulting phenylurethane crystallised from light petroleum in stout prisms, about 1 cm. long, melting at about 64° . The phenylisocyanate was split up by boiling it for several hours with alcoholic potash and the resulting alcohol driven off with steam. In order to remove the aniline which had also been formed in the process of decomposing the ester, the distillate was shaken up with tartaric acid solution. The alcohol prepared by this method boiled at 199 to 200° and gave: d_{150} 0,8666, $\alpha_D - 17^{\circ} 41'$, n_{D200} 1,46238, mol. refr. found 49,12, calc. as $C_{10}H_{18}O_{1/2}$ 48,97.

Treated with phenylisocyanate, the alcohol reverted into the phenylurethane, m. p. 64° ; when oxidised with bichromate and sulphuric acid it reverted into citral.

Hence the specific gravity of linalool is lower than has hitherto been assumed to be the case. (We have observed d_{150} 0,869 to 0,873 in the commercial article¹⁾). It should also be stated here that Tiemann²⁾ has found similar constants in a specially purified linalool: b. p. 86 to 87° (14 mm.), d_{200} 0,8622, n_{D200} 1,46108.

On β -cyclohexanol- d -glucoside see p. 139.

Borneol. J. Aloy and V. Brustier³⁾ have found that when borneol-vapours are passed over copper oxide heated to from 250 to 300° , camphor is formed. At 300° the reaction is quantitative. When the temperature is further increased the yields diminish until finally, at between 420 and 430° , a mixture of terpene hydrocarbons results. But, reversely, camphor cannot be reduced to borneol by Sabatier's and Senderens's reduction method. The reduction, however, may be accomplished with camphor oxime, by passing the oxime-vapours, mixed with hydrogen, over nickel heated to about 180 to 200° . In the course of this conversion bornylamine, dibornylamine and camphylamine are generated in addition to ammonia.

¹⁾ Gildemeister and Hoffmann, *Die ätherischen Öle*, 2nd Ed., Vol. I. p. 370.

²⁾ Berl. Berichte **31** (1898), 834.

³⁾ Bull. Soc. chim. IV. **9** (1911), 733.

Isoborneol. Semmler and E. W. Mayer¹⁾ have ascertained that camphene, when boiled with formic acid in a reflux-condenser, is converted quantitatively into *isobornyl* formate. 20 g. Camphene yielded 24 g. formate. The ester gave the following constants: b. p. 91 to 93° (11 mm.) $d_{20} 1,005$, $n_D 1,4726$.

Thujyl Alcohol. Paolini²⁾ reports on experiments in the preparation in the pure form of one of the isomeric thujyl alcohols. Several investigators have obtained isomeric thujyl alcohols by reducing the several thujones according to various methods, as well as by reducing sabinol, but nothing has been reported concerning the separation of these alcohols. When the ketone of thuja oil or of tansy oil (which, according to Wallach, is a mixture of a large proportion of α - with a small proportion of β -thujone and *vice versa*), is reduced, the result is a mixture of two isomeric alcohols corresponding to the two ketones, not taking in account that owing to the appearance of a new asymmetric carbon-atom during the process of reduction, a fresh source of isomerism has been opened up. The rotation ascertained by the several investigators varies: Kondakoff gives $[\alpha]_D + 45^\circ 57'$, Tchugaeff, $[\alpha]_D + 69^\circ 49'$, which shows that the alcohols obtained in the process of reduction are not absolutely identical, a fact which points to the presence of an isomeric alcohol which is optically either *lævorotatory* or, — but more faintly — *dextrorotatory*. Semmler has observed, moreover, that when "thujyl alcohol" is oxidised, the ketone which it yields is not quite the same as the fundamental ketone, its rotatory power being less than that of latter, and Tchugaeff's observations on the formation of two thujenes from tanacetyl alcohol by his xanthogenate-method have confirmed the conclusion that the bodies in question are isomeric alcohols. Paolini has tried, by means of acid phthalic ester, to split up the tanacetyl alcohol which is obtained from β -thujone by reducing it with sodium and alcohol. The crude phthalate appeared as a semi-liquid, sticky mass, very readily soluble in most of the organic solvents and capable of purification by repeated solution in benzene and precipitation with an abundance of light petroleum. Final recrystallisation from light petroleum afforded an ester acid which might be regarded as a uniform body, as the m. p. (120°) showed no further increase. The rotation of the ester acid, of which the silver-, the calcium-, and the strychnine-salts were prepared and analysed, was in a solution of 1,0956 g. of the substance in 100 cc. absolute alcohol $+ 2^\circ 0'$ in a 2 dm.-tube; which gives $[\alpha]_D + 91^\circ 27'$. When the ester acid was saponified during half an hour in a water bath, it yielded the free alcohol, constants: b. p. 206°, $d_{20} 0,9229$, $\alpha_D + 105^\circ 50'$, $n_{D16} 1,4625$.

¹⁾ Berl. Berichte 44 (1911), 2012.

²⁾ Rendiconti della R. Accademia dei Lincei. Vol. 20, 1st Semester, No. 10, p. 765. Meeting of 21st May 1911. From a reprint kindly sent to us.

Treatment of the alcohol with phthalic anhydride yielded the same acid phthalate, m. p. 120° ; oxidation with chromic acid gave rise to a ketone, of which the semicarbazone possessed the following constants: m. p. 174 to 175° , α_D of a solution of 1,0816 g. substance in 100 cc. absolute alcohol, $+4^{\circ}46'$ in a 2 dm.-tube; from which $[\alpha]_D + 200^{\circ}$ was calculated.

Menthenol. B. D. W. Luff and Perkin¹⁾, after overcoming serious experimental difficulties, have succeeded in resolving into its optical components *d,l*-1-methyl- Δ^3 -cyclohexene-3-carboxylic acid²⁾ by repeated crystallisation of its brucine and *l*-menthylamine salts. It is still doubtful whether the active modifications have been obtained in a chemically pure state, the yields being rather small. *d*-1-methyl- Δ^3 -cyclohexene-3-carboxylic acid melts at 62 to 64° ; $[\alpha]_D + 40,1^{\circ}$ (3,6% solution in ethyl acetate). The ethyl ester boils at 150 to 151° (100 mm.); $[\alpha]_D + 32,5^{\circ}$. The dibromo-derivative of the free acid (m. p. 165° ; $[\alpha]_D + 28,5^{\circ}$) when treated with potassium hydroxide does not give off hydrobromic acid but only bromine, the original acid with the same optical deviation being recovered in the process. When magnesium methyl iodide is allowed to act upon ethyl *d*-1-methyl- Δ^3 -cyclohexene-3-carboxylate, the result is *d*- Δ^3 -*m*-menthenol-8 (b. p. 107 to 108° at 25 mm.; $d_{20}^{20} 0,9235$; $[\alpha]_D + 20,9^{\circ}$ in 3,6% solution in ethyl acetate; $n_D 1,4791$); this substance, when heated with oxalic acid, yields *d*- $\Delta^{3:8(9)}$ -*m*-menthadiene: b. p. 179° (730 mm.), $[\alpha]_D + 17,5^{\circ}$ (3,5% solution in ethyl acetate), $n_D 1,4975$.

l-1-methyl- Δ^3 -cyclohexene-3-carboxylic acid gave $[\alpha]_D - 35,8^{\circ}$ (3,7% solution in ethyl acetate); its ethyl ester boiled at 148 to 150° (100 mm.): $[\alpha]_D - 28,9^{\circ}$. The constants of *l*- Δ^3 -*m*-menthenol-8 were as follow: b. p. 102 to 103° (14 mm.), $[\alpha]_D - 18,5^{\circ}$ (4% solution in ethyl acetate). It yielded *l*- $\Delta^{3:8(9)}$ -*m*-menthadiene: b. p. 181 to 182° (760 mm.), $[\alpha]_D - 12,9^{\circ}$ (4% solution in ethyl acetate), $n_D 1,4969$.

Perkin, in collaboration with Tsan Quo Chou³⁾ also describes a dextro-rotatory modification of the Δ^3 -*p*-menthenol-8⁴⁾ and $\Delta^{3:8(9)}$ -*p*-menthadiene described by Perkin and Wallach. The authors started from *d*-1-methylcyclohexane-3-one, which was allowed to react with sodium amide and carbonic acid. The product of reaction, *d*-1-methylcyclohexane-3-one-4-carboxylic acid, when reduced with sodium amalgam yielded *d*-1-methylcyclohexane-3-ol-4-carboxylic acid, which when treated with phosphorus trichloride gave rise to *d*-1-methyl- Δ^3 -cyclohexene-4-carboxylic acid. For the purpose of preparing *d*- Δ^3 -*p*-menthenol-8 the ethyl ester of *d*-1-methyl- Δ^3 -cyclohexene-4-carboxylic acid was allowed to react with magnesium methyl iodide. The alcohol possessed the following properties: b. p. 105°

¹⁾ Journ. chem. Soc. **99** (1911), 518.

²⁾ Comp. Report April **1911**, 175.

³⁾ Journ. chem. Soc. **99** (1911), 526.

⁴⁾ Comp. Report October **1910**, 190.

Neroli Oil. $d_{15^{\circ}}$ 0,870 to 0,880; $\alpha_D + 1$ to $+ 6^{\circ 1}$); sap. no. 20 to 52^2).

¹⁾ We have met with genuine samples which showed up to $+ 8^{\circ}$.

²⁾ In the course of the last few years we have met with pure oils of which the sap. no. was as high as 55.

Orange Oil, bitter. $d_{15^{\circ}}$ 0,848 to 0,854; $\alpha_{D20^{\circ}} + 92$ to $+ 98^{\circ 1}$).

¹⁾ Neither the values given above for the rotation nor those relating to the sp. gr. are in accord with the facts. The limits of value are as follows: $d_{15^{\circ}}$ 0,853 to 0,857, $\alpha_{D20^{\circ}} + 90$ to $+ 93^{\circ}$.

Orange Oil, sweet. $d_{15^{\circ}}$ 0,846¹⁾ to 0,853; $\alpha_{D20^{\circ}} + 95$ to $+ 99^{\circ}$.

¹⁾ We have never found the sp. gr. to fall below 0,848.

Peppermint Oil.

1. English. $d_{15^{\circ}}$ 0,900 to 0,910; $\alpha_D - 22$ to $- 33^{\circ}$; total menthol 55 to 66%, free menthol 50 to 60%, esterified menthol 5 to 16%.

2. American. $d_{15^{\circ}}$ 0,900 to 0,920; $\alpha_D - 25$ to $- 33^{\circ}$; total-menthol 50 to 64%, free menthol 40 to 55%, esterified menthol 10 to 24%.

3. French. $d_{15^{\circ}}$ 0,910 to 0,926; $\alpha_D - 6$ to $- 16^{\circ 2}$); total-menthol 45 to 58%, free menthol 40 to 52%, esterified menthol 5 to 10%.

4. Japanese, dementholised. $d_{15^{\circ}}$ 0,894 to 0,900³⁾; $\alpha_D - 25$ to $- 35^{\circ}$; total menthol 45 to 70%, free menthol 40 to 65%, esterified menthol 3 to 13%⁴⁾.

¹⁾ The minimum limit is incorrect; it should be reduced to $- 18^{\circ}$.

²⁾ We have met with French oil down to $- 35^{\circ} 18'$. Comp. Report April 1905, 62.

³⁾ The sp. gr. of the oils of commerce ranges up to 0,905.

⁴⁾ As we informed the Committee at the time, we regard the giving of separate values for total menthol, free menthol and esterified menthol as quite unnecessary, and as needlessly complicating the examination. In our view it would be sufficient to indicate the content of total menthol, *i. e.* the value shown by the sap. no. of acetylated oil. It is true that by doing this the portion of menthol which occurs in the oil in the esterified state is disregarded, but the values obtained can only be too high to the extent of about 3%, and are therefore quite accurate enough for practical purposes. If it is desired to determine the content of total menthol taking into account the ester content, this can be done by the method described on p. 139. Our own experience of the menthol content of the various peppermint oils is somewhat at variance with the data given above. We have found the limits of value to be as follows: —

	Total menthol (not taking into account the ester content)	Ester menthol
English Oil	51 to 66%	3 to 16%
American Oil	48 „ 64%	3 „ 14%
French Oil	45 „ 69%	5 „ 21%
Japanese dementholised Oil . . .	45 „ 60%	3 „ 13%

The data supplied by the Association which relate to the menthol content of the several varieties of oil, especially those referring to free and esterified menthol cannot, in our opinion, be regarded as accurate.

Rose Oil. d_{20° 0,855 to 0,865¹⁾; sol. p. $+ 17$ to $+ 23^\circ$.

¹⁾ This statement appears to have been borrowed from the French Codex, but as rose oil is often in a state of congelation at 20° it is desirable to carry out this determination at a higher temperature. At 30° (calculated for water of 15°) the limits of value observed by us ranged from 0,849 to 0,862.

Rosemary Oil. d_{15° 0,900 to 0,920; $\alpha_D + 5$ to $+ 15^\circ$ ¹⁾; soluble in one-half its weight of 90 per cent. alcohol.

¹⁾ The minimum limit is not correct, many rosemary oils have a lower rotation.

Rue Oil. d_{15° 0,833 to 0,850; α_D faintly to the right; sol. p. $+ 7$ to $+ 10^\circ$ ¹⁾.

¹⁾ Very many Algerian oils of rue only congeal in a freezing mixture and are faintly lævorotatory.

Sandalwood Oil. d_{15° 0,975 to 0,985; $\alpha_D - 10$ to $- 20^\circ$, sap. no. should not exceed 25; santalol ($C_{15}H_{24}O$) not less than 90⁰/₀; sol. at 20° 1 vol. in 5 of 70 per cent. alcohol.

Savin Oil. d_{15° 0,909 to 0,930; $\alpha_D + 35$ to 60° ; sap. no. 107 to 125.

Star Anise Oil. d_{20° 0,980 to 0,990; α_D faintly to the left, not to the right¹⁾; sol. p. $+ 14$ to $+ 18^\circ$; anethol content 80 to 90⁰/₀; sol. 1 vol. in $1\frac{1}{2}$ to 6 of 90 per cent. alcohol²⁾.

¹⁾ Occasionally star anise oils are met with which are faintly dextrorotatory.

²⁾ Star anise oil is soluble with $1\frac{1}{2}$ to 3 vols. of 90 per cent. alcohol.

Thyme Oil. A thick¹⁾, reddish-brown oil; d_{15° 0,900 to 0,950; phenol content 18 to 65⁰/₀; sol. 1 vol. in 2 of 80 per cent. alcohol.

¹⁾ The adjective "thick" gives a wrong impression of the consistency of thyme oil.

Wintergreen Oil. d_{15° 1,179 to 1,190; $\alpha_D \pm 0^\circ$ or faintly lævorotatory.

Wormwood Oil. d_{15° 0,901 to 0,955; sol. 1 vol. in 2 to 4 of 90 per cent. alcohol¹⁾.

¹⁾ The oils at first give a solution with any proportion of 90 per cent. alcohol; but on further dilution opalescence to cloudiness frequently ensues.

triphenylmethane derivatives by the condensation of aromatic aldehyde with hydroxyhydroquinone trimethylether. For instance, with benzaldehyde he obtained 2,4,5,2',4',5'-hexamethoxytriphenylmethane (m. p. 130,5°) with vanillin 4-hydroxy-3, 2',4',5',2'',4'',5''-heptamethoxytriphenylmethane (m. p. 187,5°), with salicylic aldehyde 2-hydroxy-2',4',5',2'',4'',5''-hexamethoxytriphenylmethane (m. p. 176°), with piperonal 3,4-methylene dihydroxy-2',4',5',2'',4'',5''-hexamethoxytriphenylmethane (m. p. 137°) and from asaric aldehyde tris-(2,4,5-trimethoxyphenyl)methane (m. p. 184°).

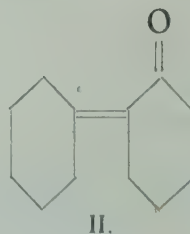
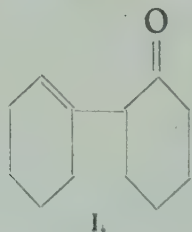
The last-named body is identical with the compound which has been prepared by Széki and Fabinyi from asaric aldehyde by heating it with hydrochloric acid¹⁾.

Ketones.

Methylheptenone. Prileshajew²⁾ has prepared an oxide of methylheptenone by treating the ketone with benzoylhydroperoxide, in the manner described by us in an earlier Report³⁾. The methylheptenone oxide $C_8H_{14}O_2$ constitutes a liquid with a terpene-like odour; b. p. 68 to 70 (50 mm.); 146,5 to 147,5° (746 mm.) which yields a glycol $C_8H_{14}O(OH)_2$ with water: m. p. 65 to 66°, b. p. 139 to 140° (13 mm.), d_{40}^{100} 1,0698, d_{40}^{160} 1,0582, $n_{D_{16,20}}^{160}$ 1,4610. By eliminating water, the glycol is made to yield a diketone $C_8H_{14}O_2$ (b. p. 94 to 95° at 15 mm.; d_{40}^{160} 0,9396) of which the monosemicarbazone melts at 197 to 198°, m. p. of the dioxime 131,5 to 132°. In the process of oxidising the methyl heptenone an isomeric oxide was discovered as a by-product; this oxide yields with water a glycol possessing the following properties: b. p. 143 to 145° (14 mm.), d_{40}^{160} 1,0583. When water is split off from the glycol it yields the diketone described above.

Cyclohexenehexanone. In our last Report⁴⁾ we mentioned briefly that Wallach, while reducing cyclohexenehexanone had obtained cyclohexenehexanol, which alcohol is capable of being oxidised into a glycerol and a ketonic acid. Further particulars of this method are given in his 106th paper on Terpenes and Essential Oils⁵⁾.

It is probable that cyclohexenehexanone is constructed according to formula I shown below. Formula II with a semicyclic double bond is: —



¹⁾ Comp. Report April 1911, 180.

²⁾ Journ. russ. phys. chem. Ges. 43 (1911), 609. Quoted from Chem. Zentralbl. 1911, II. 268.

³⁾ Comp. Report April 1910, 153.

⁴⁾ Report April 1911, 165.

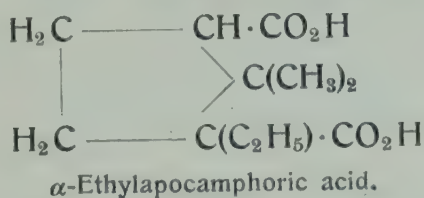
⁵⁾ Liebigs Annalen 381 (1911), 95.

When *cyclohexylhexanone* is oxidised with chromic acid in glacial acetic acid it yields a ketonic acid of the formula $C_{12}H_{20}O_3$ (m. p. 58°). This acid is probably a δ -hexahydrobenzoyl-*n*-valeric acid. Upon heating its methyl ester with sodium in toluene, a compound $C_{12}H_{18}O_2$, b. p. 150° (11 mm.), was obtained, which is probably a diketone. No semicarbazone was obtained, but the methylated compound yielded a semicarbazone melting at 203° .

Menthone. A paper by A. Mailhe and M. Murat¹⁾ on the reduction of cyclic oximes by means of hydrogen in the presence of nickel, also refers to *l*-menthone oxime, (m. p. 59° ; $[\alpha]_D -42,51^\circ$). The reduction of the oxime was accomplished at about 280° , the reaction-products being menthylamine and dimethylamine $(C_{10}H_{19})_2NH$, of which latter body the hydrochloride melts, with decomposition, at 207° .

Camphor. In our last Report²⁾, we referred to Komppa's rejoinder to the attacks by Blanc and Thorpe³⁾ upon the synthesis of camphoric acid. Komppa, in collaboration with O. Routala⁴⁾, has published a further note on the same subject, in which he gives a total synthesis of ethylapocamphoric acid. This interesting paper, to which we are unable to refer in detail for want of space, again shows that the statements of Blanc and Thorpe are untenable.

Komppa and Routala obtained α -ethylapocamphoric acid both in the *cis*- and the *trans*-modification. The former occurs in the form of small prisms, m. p. $183,5$ to 184° ; the latter was only obtained in an oily state.



Methylaurenone. von Baeyer and Villiger⁵⁾, in the course of a reaction of Caro's sulphuric acid on camphor, had obtained, in addition to α -campholide, a lactone $C_{10}H_{16}O_4$, m. p. 189 to 191° . R. Locquin⁶⁾ has subjected this lactone to closer investigation. Upon heating it with dilute sulphuric acid or phosphoric acid in a sealed tube, he obtained an inactive, unsaturated ketone $C_9H_{14}O$, possessing the following characteristics: b. p. 82 to 86° (10 mm.), 95 to 96° (18 mm.), $d_{40}^{100} 1,062$. With semicarbazide the lactone yields a mixture of two semicarbazones, melting respectively at 198 and 150° .

¹⁾ Bull. Soc. chim. IV. 9 (1911), 467.

²⁾ Report April 1911, 182.

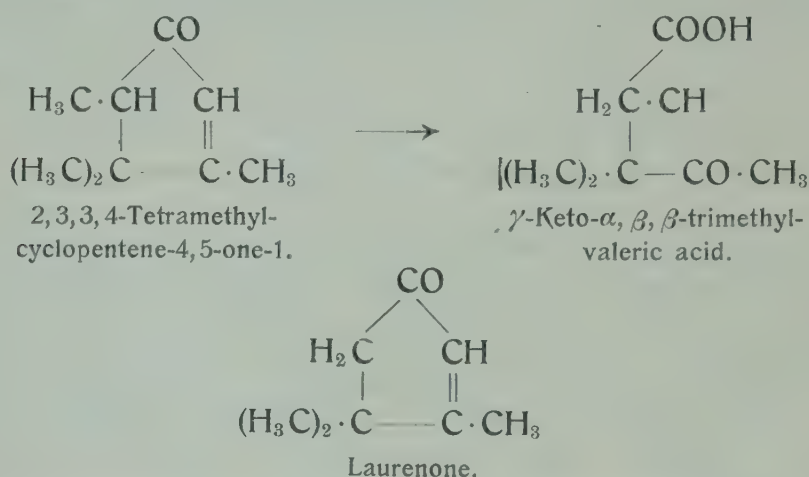
³⁾ Report October 1910, 196.

⁴⁾ Berl. Berichte 44 (1911), 858.

⁵⁾ Berl. Berichte 32 (1899), 3625.

⁶⁾ Compt. rend. 153 (1911), 284.

The oxime boils between 122 and 128°, when the liquid is allowed to stand for a long time, crystals (m. p. 95 to 96°) are precipitated. When subjected to oxidation with permanganate of potassium it gives γ -keto- α, β, β -trimethyl valeric acid, $\text{CH}_3 \cdot \text{CO} \cdot \text{C}(\text{CH}_3)_2 \cdot \text{CH}(\text{CH}_3) \cdot \text{COOH}$, of which the ethyl ester boiled between 105 and 107° (12 mm.). The semicarbazone of the ethyl ester melts at 158 to 159°. When oxidised with sodium hypochlorite, γ -keto- α, β, β -trimethyl valeric acid yields trimethyl succinic acid, $\text{COOH} \cdot \text{C}(\text{CH}_3)_2 \cdot \text{CH}(\text{CH}_3) \cdot \text{COOH}$ (m. p. 152°). This shows the ketone $\text{C}_9\text{H}_{14}\text{O}$ to be 2,3,3,4-tetramethyl cyclopentene-4,5-one-1: —



When the ketone is reduced with sodium in absolute alcohol there results 2,3,3,4-tetramethyl cyclopentanol-1 (b. p. 87° at 10 mm.; m. p. of the phenylurethane 113 to 114°). The corresponding ketone, 2,3,3,4-tetramethyl cyclopentanone, boils at 178 to 180°.

As Tiemann¹⁾ has already given the name of laurenone to the ketone of the structure given below, it is necessary to assign to tetramethyl cyclopentenone the name of α -methyl laurenone.

On the specific rotation of camphor, see p. 123.

On the determination of camphor as oxime, see p. 121.

On the reduction of camphor and camphor oxime, see p. 141.

Epicamphor. Two keto-derivatives are derivable from camphane, *viz.*, ordinary camphor (I), and a derivative (II) which F. R. Lankshear and W. H. Perkin jun.²⁾ propose to call *epicamphor*. For the purpose of preparing this isomeride of camphor, camphor carboxylic acid (III) is converted into bornylenecarboxylic acid (IV) by reduction and subsequent elimination of water. When reduced with palladium and hydrogen, this acid is converted quantitatively into camphane carboxylic acid (V). This saturated acid is readily brominated by warming its chloride with bromine

¹⁾ Berl. Berichte 33 (1900), 2950.

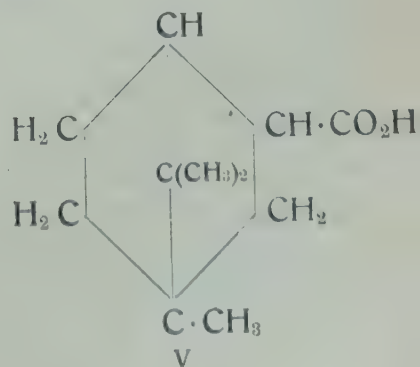
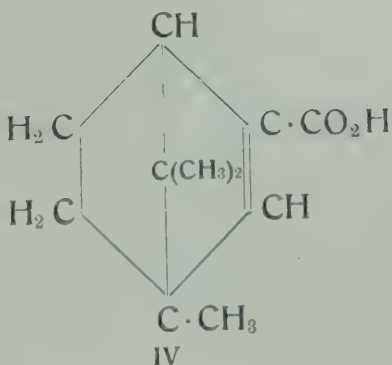
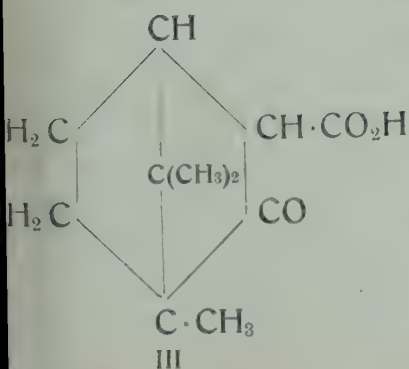
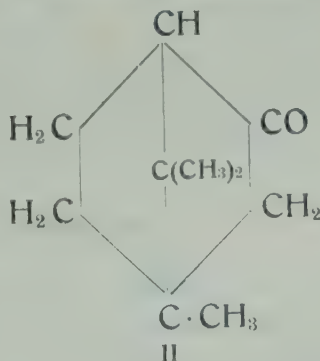
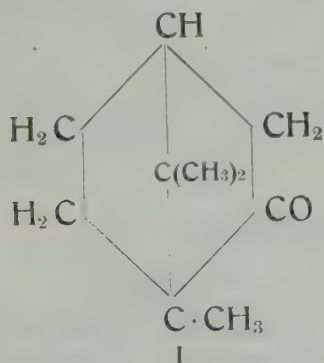
²⁾ Proceed. chem. Soc. 27 (1911), 166.

on the steam-bath. The bromo-ester obtained by pouring the bromo-acid chloride into alcohol, was digested by the authors with potassium acetate in acetic acid solution. The reaction-product was hydrolysed with alcoholic potash liquor, α -hydroxycamphane carboxylic acid (VI) being formed in the process. This acid, when oxidised with peroxide of lead, permanganate, or chromic acid, gave a small yield of *epicamphor* (II).

Epicamphor volatilises readily with steam and possesses the same odour as camphor. The m. p. was found to be 165° , but the authors intend to repeat this determination as soon as they have a larger quantity of the substance at their disposal. The oxime of *epicamphor* melts at 102° , and the semicarbazone between 225 and 227° .

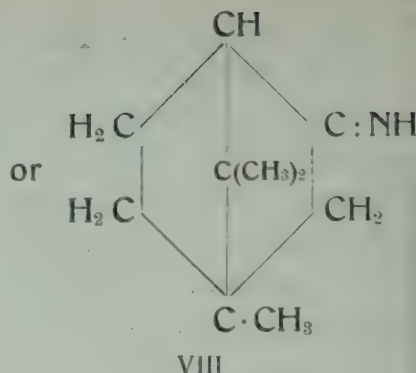
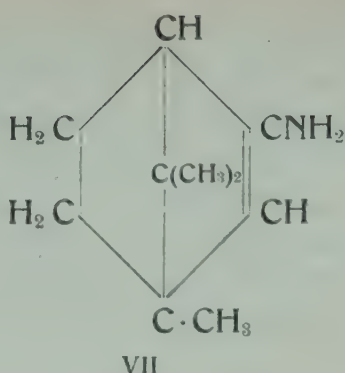
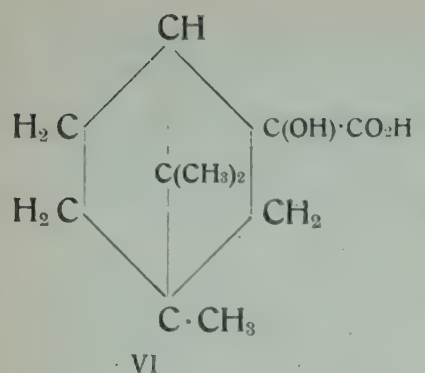
J. Bredt and W. Hilbing¹⁾ are of opinion that *epicamphor* is identical with the β -camphor prepared by them. These authors took as their starting-material bornylenecarboxylic acid, the chloride of which (b. p. 114 to 115° at 14 mm.) they converted into the semicarbazide²⁾ by treating it with hydrazine hydrate, the semicarbazide being subsequently converted by Curtius' method into the azide. By Curtius' conversion method they obtained from the azide, aminobornylene (VII) or β -camphorimine (VIII) which was converted by boiling with acid into the corresponding camphor, *viz.*, β -camphor (II) (bornylone). The constants of β -camphor are as follow: m. p. 181 to 182° (184 to 185° after purification from primarily produced semicarbazone), b. p. $213,1$ to $213,4^{\circ}$. β -Camphoroxime has m. p. 237 to 238° . With nitric acid β -camphor is oxidised into β -camphoric acid.

β -Camphor is rather more volatile than ordinary camphor.



¹⁾ Chem. Ztg. 35 (1911), 765.

²⁾ This should probably be acid hydrazide.



Carvone. As in the case of limonene (see p. 138), G. Vavon¹⁾ has observed several phases when reducing d-carvone with platinum and hydrogen. In this case also, observation of the rotation indicates the extent to which the process of reduction has progressed and it is therefore possible readily to isolate the various reduction-products. The first reduction-product obtained by Vavon was d-carvotanacetone: b. p. 227 to 228°, d_{40}^{180} 0,937, $[\alpha]_{578} + 59,8^\circ$, $n_{D20} 1,4817$. Further progress of the reduction led to tetrahydrocarvone: b. p. 218 to 219°, d_{40}^{200} 0,904, $[\alpha]_{578} - 27^\circ$, $n_{D20} 1,4555$. Finally, Vavon obtained carvomenthol: b. p. 217 to 218°, d_{40}^{200} 0,908, $[\alpha]_{578} - 24,7^\circ$, $n_{D20} 1,4648$. The acetate of carvomenthol is a liquid with a pleasant odour, b. p. 230 to 231° (d_{40}^{200} 0,928; $[\alpha]_{578} - 27,6^\circ$; $n_{D20} 1,4477$); the benzoate possesses the following constants: b. p. 185 to 186° (15 mm.), d_{40}^{200} 1,006, $[\alpha]_{578} - 12,9^\circ$, $n_{D20} 1,509$.

Vavon has not only reduced carvone, but a whole series of other ketones and aldehydes into their corresponding alcohols by means of hydrogen in the presence of platinum. The substances so treated include acetone, methylethylketone, benzophenone, *cyclohexanone*, valeric aldehyde, *cænanthol*, benzaldehyde, vanillin, piperonal, and anisic aldehyde.

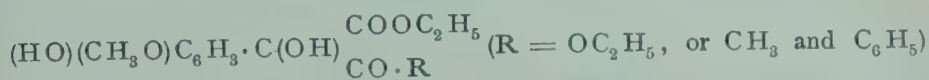
Phenols and Phenolethers.

A. Angeli, L. Alessandri and R. Pegna²⁾ are engaged on research into the action of nitroso derivatives, and especially of nitroso benzene, upon unsaturated compounds. Like dihydroxyammonia $\text{NH}(\text{OH})_2$, nitrosobenzene $\text{C}_6\text{H}_5\text{NO}$, the phenyl ether of anhydrous dihydroxy ammonia $\text{H}\cdot\text{NO}$, reacts upon double bonds. In this capacity nitrosobenzene was tested for its behaviour towards certain allyl and propenyl compounds. It was found to dissolve only slowly in anethol and in *isosafrol* (both propenyl derivatives), forming a brown liquid from which no characteristic bodies were obtainable. Combinations with allyl groups, as for example safrol and eugenol ethyl ether, afforded well-defined reaction-products. Safrol reacted

¹⁾ Compt. rend. 153 (1911), 68.

²⁾ Rendiconti della R. Accad. dei Lincei Vol. 19, Ser. 5, 1st Half-year, no. 10, p. 650. Meeting of 22nd May, 1911. From a reprint kindly sent to us.

of zinc, with mesoxalic ester or with the α, β -diketocarboxylic esters, of which the constitution is similar, such as acetyl- or benzoyl-glyoxylic ester, afterwards heating it for several hours to about 50° . After diluting the solution with water, shaking with ether, and washing the ether with soda-solution, any unchanged guajacol is removed by means of steam and the condensation product: —



recovered in the crystalline form. By oxidation with acetate of copper at 80° these compounds can be quantitatively converted into vanilloyl-carboxylic acid, but, as regards the mesoxalic ester derivative, this can be obtained only after saponification and boiling with copper chloride. From the acid referred to, dimethyl-p-toluidin, at 170° , splits off almost quantitatively carbon dioxide and, in contradistinction to other vanillin-processes, the result is a very pale vanillin which is free from isomerides and from resinous substances. It is not recommended to employ for the purposes of synthesis the free ketonic acids in lieu of the esters, because the former are much less stable. Even when the relatively stable dioxo-succinic acid, (of which the sodium-salt is used technically in the preparation of the yellow dye known as tartrazine), is liberated from the salt by means of sulphuric acid, and this solution is shaken with guajacol, only 15% of the guajacol used is recovered in the form of vanilloyl-carboxylic acid.

are split up into nitrosobenzene and the corresponding aldehyde; when air is excluded the compound from cinnamic aldehyde is partly re-converted into cinnamic aldehyde, but in addition to this the greater part of it, with elimination of oxygen, yields the Schiff's base $R \cdot CH:N \cdot C_6H_5$, together with smaller quantities of other, but indefinable, products. When exposed to air, on the other hand, the phenyl ether from benzaldehyde is re-converted into the aldehyde and also yields nitrosobenzene, together with small proportions of azoxybenzene, o-hydroxyazobenzene, and dibenzaniline.

Anethol. Balbiano and Paolini¹⁾ on the one side, Tiffeneau and Daufresne²⁾ on the other, had investigated the behaviour of anethol glycol (prepared from anethol with mercuric acetate) when treated with dehydrating agents, such as 20% sulphuric acid or chloride of zinc. The results of the investigations were contradictory, Balbiano and Paolini asserting that p-methoxy cinnamic aldehyde is generated as the product of reaction, whereas the French investigators had obtained anise ketone. Balbiano, in a rejoinder³⁾, had cast doubt upon the last-named statement, and had declared the aforementioned aldehyde to be the sole product of reaction. In order to clear the matter up, Paolini⁴⁾, the former collaborator with Balbiano, has entered the lists with the assertion that both the aldehyde observed by Balbiano and the ketone obtained by Tiffeneau and Daufresne are generated side by side when anethol glycol is dehydrated. Paolini lays bare the defective nature of the conclusions drawn by Balbiano in his rejoinder; pointing out, for instance, that the ensuing of a red coloration with magenta-sulphurous acid is not of itself a proof of the exclusive presence of the aldehyde, and also that the melting points of the dehydration-products obtained by Balbiano differ considerably (by 8 to 9°) from those observed by other authors, which circumstance had been convincingly explained by Tiffeneau and Daufresne on the same lines as those given by Paolini. According to Paolini, the reason for the existing difference of opinion is that when the aldehyde which is supposed to be the sole product of reaction is treated with Piloty's acid for the purpose of preparing the hydroxamic acid according to Angeli-Rimini's method, a portion of the aldehyde does not enter into reaction, and that this oil-portion contains the ketone which has been overlooked by Balbiano. This ketone may be separated from the ketone of the aldehyde by means of the sparingly-soluble semicarbazone. Angeli-Rimini's reaction should not only have been carried out with the direct product of dehydration or with the oil which was recovered on the first

¹⁾ Comp. Report April 1903, 83; April 1904, 100; April 1906, 99.

²⁾ Comp. Report October 1907, 169.

³⁾ Comp. Report April 1909, 137.

⁴⁾ Rendiconti della R. Accademia dei Lincei, Vol. 20, 1st Semester, no. 12, p. 940, Meeting of 18th June, 1911. From a reprint kindly sent to us.

treatment, but also with the product regenerated from the semicarbazone melting at 175 to 176°. Had Balbiano done this, he would have identified the last-named body as being the aldehyde, and not the ketone. The fact that he omitted to do so might easily have resulted in throwing discredit upon Angeli-Rimini's reaction, which is entirely restricted to aldehydes. Paolini has again dehydrated the β -glycol of anethol under precisely the same conditions as observed by the French authors, and has obtained pure anise ketone which did not respond to Angeli-Rimini's reaction. Precisely the same was the case when, under identical conditions, *isosafrol* glycol was warmed on the water-bath for 3 to 4 hours with 20% sulphuric acid: — here also the only reaction-product was the ketone, piperonyl acetone. But with chloride of zinc at 130°, or with prolonged boiling with 20% sulphuric acid, a little aldehyde (perhaps 5%) always results in addition to the ketone. It is obvious that Balbiano had not conducted his experiments under the same conditions as observed by Tiffeneau and Daufresne, but that he had continued to apply heat for a longer time than they, and therefore obtained a reaction-product which gave the Angeli-Rimini reaction (and must therefore be regarded as an aldehyde), and also a semicarbazone which he (Balbiano) erroneously regarded as a derivative of the same aldehyde, whereas in truth it was derived from anise ketone (m. p. 184°).

Dihydroanethol. H. Thoms and W. Drauzburg¹⁾ state that when a mixture of equal parts of dihydroanethol and glacial acetic acid is heated on the water-bath with a mixture of equal parts of nitric acid of 45% and glacial acetic acid, a violent reaction takes place. The following are the products of conversion: anisic acid, anisic aldehyde, a mononitro-derivative of dihydroanethol (1-propyl-3-nitro-4-methoxybenzene, sol. p. —6°), and a dinitrophenol, probably 1-propyl-3,5-dinitro-4-hydroxybenzene, m. p. 46°.

Elemicin. Some years ago Semmler²⁾ noticed that the methoxyl-group of elemicin which stands in the para-position can be eliminated by means of nascent hydrogen. Since then, Thoms and Siebeling³⁾ have attempted also to eliminate the methoxyl-group of other phenol ethers by means of nascent hydrogen, but without success. These authors have experimented with anethol, dihydroanethol, *m*-propylphenolether, methyl*iso*-eugenol, asarone, and dihydroasarone.

Only in the case of methyl*iso*eugenol could a slight elimination of methyl be observed, giving rise to the formation of a phenol. But with

¹⁾ Berl. Berichte 44 (1911), 2125.

²⁾ Berl. Berichte 41 (1908), 2556; Report November 1908, 52.

³⁾ Berl. Berichte 44 (1911), 2134.

pyrogallol trimethylether the authors succeeded, by reacting with sodium in alcoholic solution, to eliminate without trouble a methoxyl-group, with formation of resorcinol dimethylether.

Acids.

In order to be in a position to compare the physical properties of the methylesters of monocyclic dicarboxylic acids, F. W. Semmler and E. W. Mayer¹⁾ have prepared several such esters. The dimethyl ester of *isofenchone* carboxylic acid has the following constants: b. p. 131 to 132° (14 mm.), d_{20}° 1,0515, α_D — 19°, n_D 1,4540. Camphoric dimethylester boiled at 137 to 139° (14 mm.) (149,5° at 11 mm. and 155° at 15 mm. according to Brühl and Braunschweig²⁾). α -Tanacetogene dicarboxylic dimethylester has the following constants: b. p. 129 to 130° (15,5 mm.), $d_{20}^{28} 1,0525$, α_D — 148°, n_D 1,4510. β -Methyladipic dimethylester is a liquid with b. p. 122 to 122,5° (18 mm.); d_{20}° 1,0372; n_D 1,4336.

Nitrogenous bodies.

On the occurrence of hydrocyanic acid, see p. 124.

On the determination of hydrocyanic acid, see p. 121.

On the occurrence of indole and scatole, see p. 124.

¹⁾ Berl. Berichte 44 (1911), 2011.

²⁾ Berl. Berichte 25 (1892), 1809.

SEMI-ANNUAL REPORT

OF

SCHIMMEL & Co.

(FRITZSCHE BROTHERS)

MILTITZ

NEAR LEIPZIG

LONDON & NEW YORK



OCTOBER 1912.

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List of abbreviations.

d = specific gravity.

$d_{20^{\circ}}$ = specific gravity at 20° (in references from our laboratories uniformly compared with water at 15°).

$d_{40^{\circ}}^{20^{\circ}}$ = specific gravity at 20° , compared with water at 4° .

$\alpha_{D20^{\circ}}$ = optical rotation at 20° , in a 100 mm. tube.

$[\alpha]_D$ = specific rotation.

$n_{D20^{\circ}}$ = index of refraction at 20° .

Sol. p. = solidifying point.

M. p. = melting point.

B. p. = boiling point.

n = normal.

Acid v. = acid value; ester v. = ester value; sap. v. = saponification value.

g. = gram; cc. cubic centimeter; mm. = millimeter.

Temperatures are uniformly given in degrees Centigrade.

The strength of alcohol, if not otherwise indicated, is given in per cent. by volume.

German chemical industry and conjointly with it our own branch of trade are able to look back upon a busy and successful summer. Not only was the brisk demand for consuming purposes, which had characterised the spring, maintained in every branch, but the turnover showed a continued healthy increase, while the peaceful course of international politics afforded the principal preliminary condition for the progress of the upward movement in prices which is evidently dominating the commercial situation. In many parts of Germany, however, abnormal conditions of weather have greatly disappointed the anticipations of a good harvest which were entertained earlier in the year, and this disappointment will be the more severely felt by the nation because so far there has been no abatement of the rise in the prices of food-stuffs, by which the working classes in particular are burdened. It is a matter for gratification that the balance of trade for the first half of the year clearly shows that German commerce and industry are in a flourishing condition, and it is to be hoped that the economic impediments to which we have referred, will not have too unfavourable an effect upon the autumn and winter trade, to which our industries are now looking forward. The foreign trade of the German Empire has made thoroughly satisfactory progress in the period from January to June inclusive, as compared with the corresponding period of the year 1911. Its total value amounted to 9491 million marks, as compared with 8499,3 million marks in the previous year, thus showing an approximate increase of 1000 million marks. The value of the imports amounted to 5243,6 million marks, as compared with 4818 millions in the year 1911; of the exports to 4247,4 million marks, as compared with 3681,3 millions. There has, therefore, been an increase in the first half of the year 1912 of 425,6 millions in our imports and of 566,1 millions in our exports. That our own industry has shared in this progress is evidenced by the following figures relating to the quantites by weight of merchandise exchanged with foreign countries: —

¹⁾ The introduction to the present Report and the Commercial part were written during September.

Essential Oils¹⁾:

Imports from January	1 st 1912	to June 30 th 1912,	773 500 kilos
" " "	1 st 1911	" " 30 th 1911,	746 200 "
Exports " "	1 st 1912	" " 30 th 1912,	314 700 "
" " "	1 st 1911	" " 30 th 1911,	284 900 "

German exports of artificial odoriferous compounds²⁾:

from January	1 st 1912	to June 30 th 1912,	253 900 kilos
" " "	1 st 1911	" " 30 th 1911,	239 000 "

The events in the Near East, that political barometer of Europe, should caution us against forming too optimistic a judgment of the situation, for although the prospects of an early conclusion of the peace negotiations appear to be about to be realised, it is well to be prepared for surprises. For who would have thought, a year ago, that the Turco-Italian war would be prolonged for over a twelvemonth?

It is not surprising that, owing to the favourable condition of trade, the demands upon the money-market are very heavy and that the German Imperial Bank may, ere long, find it necessary to follow the example of London and to raise its rate of discount. The increasing confidence in the investment of capital in industrial undertakings also finds expression in the remarkably low quotations of our National funds.

In the home market the sale of our manufactures might be described as being equally satisfactory in all consuming branches of industry, were it not that the cordial- and spirit-industry is adversely affected by the attitude of the Spirit-Trust. It is, however, rumoured that the leaders of the distilling-industry have recently succeeded in concluding an agreement with the Spirit-Trust, which is to come into force at the commencement of October. According to the *Zeitschrift für Spiritusindustrie* the essential points of this agreement are that the Spirit-Trust will concede to the distillers a price-rebate of 4 marks, and will set up a sliding scale of prices for future delivery for those who are prepared to contract for their requirements for the year. The distillers, in return for these concessions and in view of the security thus assured to their undertakings, are to improve the quality of their products and to raise the economic conditions industry. We hear from an authoritative source that the negotiations, of which the outcome will naturally be awaited with some eagerness, have not as yet arrived at a stage of definite conclusion.

In the month of June of the present year the shipment of our goods, particularly in Hamburg, was suddenly confronted by almost incredible difficulties, as a result of which our exports were almost brought to a standstill for a few days. It appeared that, without consulting all the

¹⁾ No. 353 b/c of the *Statistisches Warenverzeichnis*.

²⁾ No. 354 of the *Statistisches Warenverzeichnis*.

interests concerned in the matter, the German Ministry of the Interior had drawn up a set of new regulations for the "transport of dangerous articles by mercantile vessels", and that these regulations were to be accepted by the various Federal Governments, insofar as they were interested in the matter, and to be put into force. The Senate of Hamburg had passed the regulations on May 24 and had issued them in the form of an Order, to come into force on June 1st 1912. The law itself was published in the last days of May. Contrary to the Railway Traffic Regulations (upon which, however, it is mainly based), it required that every parcel of articles falling under Section III (combustible liquids), par. 9., such as essential oils, spirits of wine, liquids prepared from either of the above, &c., when dispatched in quantities of more than 40 kilos weight, must be plainly labelled "*Feuergefährlich*" ("liable to catch fire") in letters on a red background. It was further laid down that for every shipment of combustible liquids a separate Bill of Lading, in which no other articles may be entered, must be made out. This new regulation, which there was nothing to justify, was made still more irksome by an erroneous interpretation on the part of the Hamburg police-authorities, who laid it down that the 40 kilo limit referred to the gross weight and that passenger-ships were only allowed to carry a total quantity of 40 kilos of the goods in question in their hold, any excess having to be carried as deck-cargo, for which, of course, on most passenger-ships there is no room available. Fortunately, as a result of the protests which came in from all quarters, the police-authorities have withdrawn this direction, and shortly afterwards the provisions of the Order of the Hamburg Senate, insofar as they related to a number of articles, including our own, were suspended until the end of the current year. In the meantime a series of conferences has taken place in Hamburg between the Imperial commissioners and authorities and representatives of the manufacturing industries, shipping companies and associations of persons concerned in the matter, at which the subject has been thoroughly considered. We have taken part in these deliberations, and we feel justified in hoping that further discussions will lead to a result which should satisfy all the parties interested.

With regard to the general course of trade, it has to be reported in the first place that transactions have been stimulated by the many advances which have occurred in our staple articles. Clove oil, citronella oil, sandalwood oil, Italian essences, rose oil, all the geranium oils, and especially menthol have been subject to price-alterations the like of which have not been known for quite a long time and of which, in part, the end cannot as yet be discerned. The cold and damp weather of the past summer has affected particularly seriously those plants grown by us at Miltitz which are not gathered until the autumn, such as peppermint, angelica, lovage &c. The rose-crop on the other hand was gathered in June and July under the most favourable weather-conditions imaginable.

The warning which we were regretfully compelled to address in our last *Report* to those firms who, in some producing districts, threatened to demoralise the trade in certain staple articles by offering for sale notorious adulterants, has not been without success. It is true that in a few cases we were forced to threaten with the disclosure of names, but in doing so we attained our object, a fact which we desire specially to place on record here.

Before we pass on to the consideration of the various selling markets we wish to observe that in the course of last summer our workmen's colony has been enlarged by three buildings containing altogether 24 separate dwellings and that we intend next year to increase the accommodation for our staff by the erection of three other buildings which will afford dwelling-room for six chemists.

The extension of our works at Barrême (France), of which an illustration depicting the new factory appears elsewhere in this *Report*, is referred to under the heading "Lavender Oil".

In spite of the unrest which has lately been caused in the spirit-industry (the principal consumer of our manufactures), by the attitude of the Spirit-Trust, our business in Austria has been satisfactory, and our branch works at Bodenbach were able to utilise to their full extent the structural enlargements carried out last year, the more so because in the Hungarian portion of the Monarchy the demand was also extremely brisk. Those industries which use Austrian spirit have met the dictatorial behaviour of the Trust unitedly, and with admirable energy. It is true that the reductions in price which have lately been announced by the Trust are generally regarded as nothing more than a dexterous tactical move, but it is probable that in the long run the thoroughly justifiable action of the combined industries will not remain fruitless. Nothing new has been heard of the increase in the Austrian spirit tax which has already been threatened for so many years, the time of its introduction being still on the knees of the gods.

The sale of our manufactures in France continues to increase steadily and in all branches, and we are, therefore, in a position to declare once more that the increased customs duties of 1910 have had no restricting effect upon our relationship with our neighbour State, where fortunately the quality of our goods has always been properly appreciated. The difficulties experienced in passing merchandise through the French customs, to which reference has repeatedly been made in previous *Reports*, have considerably abated, from which it would appear that the authorities concerned have grown tired of unnecessary objections and superfluous correspondence, leading to nothing in the end.

Business with Italy has been but slightly affected by the war which has now lasted a full year, and the Italian commercial statistics for the first half of 1912, which are now available, are very favourable indeed.

True, the value of the imports, amounting altogether to 1803 million lire, was less by 11,5 million lire than that of the corresponding period of 1911, but this falling off is solely due to the diminished importation of agricultural produce consequent upon the favourable harvest of the year 1911. On the other hand, the exports during the first half year of 1912 reached the value of 1140 million lire, that is to say, there is an increase of 61 million lire. In the face of these statistics there is no room for doubt that, when once peace has been declared (which it is to be hoped will be soon), the country will be on the road towards a successful future, especially in view of the fact that experience shows that, after a war, trade and traffic always experience a revival. According to the published statistics the suspensions of payment in Italy have increased by more than 50 p. c., which must be regarded as an attendant phenomenon of the war. This crisis naturally operates in favour of substantial firms, because it frees the commercial community from the competition of incompetent and financially weak elements.

Since our last *Report*, commerce and industry in the United Kingdom have continued to be affected by labour unrest and by disturbances which have only been brought to a close within the past few weeks. Scarcely had the gigantic coal strike with its attendant evils been settled, and some degree of order restored out of the confusion brought about by the suspension of work, scarcely had the all but universal financial losses been overcome, although by no means forgotten, when suddenly and almost without any warning a great strike broke out at the London Docks. As in many other instances, so here, — at any rate broadly speaking, — the question at issue was not so much one of real and well-founded discontent among the labourers, as rather, in the first place, a trial of strength between the management of the docks on one side and an ultra-revolutionary group of strike-leaders on the other. The demands of these latter shouters were aimed at nothing less than the supreme control of the docks; in the future the strike-leaders alone were to determine who should be allowed to work in the docks; theirs alone was to be the right to dictate to the employers what wages should be paid, and many other things of similar character and purport. Quite naturally these impertinent demands were roundly rejected by the docks' management, with the result that the infuriated leaders left no stone unturned to enforce their dictatorial behests by violent means. In their daily agitational orations they used towards the work-givers a language which mocks all attempt at description, and which did much to bring public opinion in a solid phalanx on the side of the management. Notwithstanding this, the labour-leaders, by means of empty promises, succeeded in inducing the men to hold out, and for nearly two months close upon 100000 workmen were idle and, together with their families, condemned to a life of ever-worsening starvation, while the well-paid and well-fed leaders ("misleaders" would be a more appropriate

term), continued their agitation in the same irresponsible manner, until in the end the whole senseless movement collapsed.

In home-politics, too, the situation in the United Kingdom appears to be far from bright. The final stages of the debate on the Home Rule Bill give promise of a winter of political excitement, and the widespread agitation which is being set on foot against the Bill (a measure which is thoroughly detested in many quarters), warrant the gravest fears in certain districts, such as Ulster, unless, before their realisation, events should occur by which the Home Rule Bill is again consigned to limbo for an indefinite time. Such an event would be the fall of the Liberal Government, to accomplish which the Unionist party has recently been straining every nerve.

The fact that, in spite of all these critical conditions, our London branch house is once more able to look back upon a period of satisfactory activity, is a proof of that great elasticity of the British market to which we have already had occasion to refer in previous reports. The monthly Board of Trade Returns of Imports and Exports have throughout shown increased totals, with the exception of the month of June, which marked the culminating point of the dock strike, and in which a decrease was bound to occur, because during this period the movement of merchandise of all descriptions, with the exception of the importation of food-stuffs, was completely paralysed. In the month of August British trade again showed a considerable increase, the imports being £ 9138047 and the exports £ 7696021 in excess of those of the same month of the year 1911.

Trade with British India has continued to move within normal limits, although here and there complaints of flat markets and lack of buying enterprise were heard. We have repeatedly taken occasion to refer in our *Reports* to the fact that India is systematically flooded with rubbish, and we are still compelled, with regret, to complain of the unfair competition which we so often encounter in this market.

According to the report of the German Consul in Bombay the monsoon in Western and Central India has so far, generally speaking, taken a favourable course. At its commencement in June it was very weak and irregular, leading to serious fears for agriculture, the more so because there had also been but little rain in the previous year. But within the last few weeks the monsoon has set in very strongly, with the result that up to the present the rainfall has been sufficient and that a normal course may now be looked for. A specially favourable circumstance is that precisely in the distressed districts of Kathiawar, Gujerat and Panch Mahals, which suffered from the great drought of last year, an abundance of rain has fallen throughout the present monsoon. Generally speaking the agricultural situation, which only recently was still critical, now holds out satisfactory prospects. From all districts the reports of the condition of the crops are favourable, the crops in the cotton-growing districts

looking particularly healthy. To sum up, there is every reason, thus far, to look forward to a good harvest in 1912 13. As the purchasing power of the Indian population depends in the first place upon the result of the harvest, the course of business in the near future may be awaited with confidence.

In Australia our sales are increasing slowly but steadily, thanks to the fact that it is evidently beginning to be more and more understood there that in the end the best goods are also the cheapest. For some time a very considerable extension in the producing-powers of the local perfumery industry has been noticeable, one result of which is the reduction in the export of finished articles of perfumery, including those of German origin, and especially of soaps, to the Australian Commonwealth which is being reported in various quarters.

The *Sydney Morning Herald* publishes, on the basis of statistics published by the Customs Department, a review of the imports and exports of Australia during the first four months of the present year as compared with the same period of the six preceding years. According to this publication the imports during the first four months were as follows: —

	Merchandise £	Gold and Bullion £	Total £
1906	13 100 000	609 000	13 709 000
1907	15 844 000	453 000	16 297 000
1908	14 480 000	328 000	14 808 000
1909	15 552 000	328 000	15 880 000
1910	18 481 000	305 000	18 786 000
1911	20 771 000	583 000	21 354 000
1912	25 640 000	491 000	26 131 000

The value of the exports during the same period was as follows: —

	Merchandise £	Gold and Bullion £	Total £
1906	17 358 000	6 076 000	23 434 000
1907	22 016 000	3 089 000	25 105 000
1908	15 536 000	5 076 000	20 612 000
1909	19 489 000	2 605 000	22 094 000
1910	24 249 000	1 809 000	26 058 000
1911	21 594 000	2 403 000	23 997 000
1912	20 538 000	3 547 000	24 085 000

The above figures show that in the present year the value of the imports of merchandise for the first time exceeded that of the exports, and by a considerable amount, even the increased gold-exports having failed to restore the equilibrium of the balance of trade. The value of imports, which has steadily grown since 1908, has risen enormously in the year 1912, whereas that of the exports has steadily fallen since 1910.

So far as the results at present available go, the finances of the various States of the Commonwealth afford an equally favourable picture. These States depend for their revenues to a large extent upon the receipts

from railways and tramways. It is estimated that the total revenues of the Commonwealth and of the separate States will exceed those of the previous year (£ 56 million) by about £ 6 million, or say 11 p. c.

Both, the increased imports and the increased railway-receipts, reflect the progress which Australia enjoys as the result of a series of favourable years. All the signs, however, point to a cessation of this prosperity. The menacing drought which has prevailed since the end of last year has already wrought considerable damage and must reduce the purchasing power of the country. Hence a fall in the imports and a corresponding decline in the Commonwealth revenues are expected next year.

The political and economic conditions of Spain have unfortunately-shown no brightening since our *April Report*; on the contrary, they have grown worse. The position of the Liberal party is growing more uncertain from day to day, because Sr. Canalejas has up to the present only carried into execution by far the smallest and least important part of his whole broadly-mapped programme. A decisive crisis would probably have occurred long ago, were it not that the Conservative party decided to bide its time until Sr. Canalejas had at least settled the main problems of the religious question and had concluded the negotiations with France in respect of Morocco, the object of the Conservatives being to avoid having to grapple with these difficulties and bearing the responsibility of their solution at the very beginning of their accession to power. The eyes of the entire country are fixed upon the Hispano-French negotiations, and it would in fact appear as if Spain were unwilling to renounce, without more ado, the rights she has acquired at the cost of so much blood, and as though she were backed up by one of the other Great Powers in her resistance to the French demands. But as a result of the sacrifices made in Morocco the Spanish Government is financially exhausted, and if for no other reason than this, an agreement must be concluded within the immediate future. In the meantime all important new undertakings in the country are completely paralysed, for upon the conclusion of such an agreement the immediate and perhaps also the more distant future of Spain will depend. A slight countervailing advantage to the financial sacrifices of the war is the circumstance that the harvest in Spain promises to be exceptionally abundant this season, if the hopes are not destroyed at the eleventh hour by unfavourable climatic influences.

The other European markets give no rise for comment on the present occasion.

Our New York branch again reports very favourably on the condition of business in the United States. In the past it has generally been held that the year of a Presidential Election must always be attended by a certain degree of stagnation in commerce, caused by political agitation and by the feeling of uncertainty regarding the future of the Tariff which always accompanies the elections. But this year, in contradistinction to

these accepted views, there has not been the slightest interruption in the quiet progress of business, at least so far as our branch of trade is concerned. The pending question of the revision of the tariff on drugs and chemicals, a schedule which includes our essential oils, has been settled by a congressional vote confirming the adverse report of the Financial Committee of the Senate of 19th April last, after sufficient evidence had been collected from numerous interested parties, and this matter cannot now be reopened before the meeting of the new Congress on March 4th, 1913. Another event which particularly affected our branch of industry was the long drawn-out differences between the two parties into which those who had worked for the passing of the Federal Pure Food Law had become divided. As is well-known, these differences were settled by the resignation of Dr. Harvey W. Wiley, who since the coming into force of the law in question had been at the head of the Chemical Section of the Department of Agriculture, and who formerly presided over the Commission for the Control of Food-stuffs and Drugs. The President has not yet appointed a successor to Dr. Wiley in these important offices, but it is generally held that Dr. R. E. Doolittle is designated for the post. His appointment would be hailed with satisfaction by all who are concerned with the Pure Food Law.

Nothing special is to be said regarding the course of business which, as already stated, is developing in a thoroughly satisfactory manner; the prospects for the autumn- and winter-trade being likewise very favourable.

According to United States statistics the value of the imports of perfumery, cosmetics and other toilet-preparations during the last five years was as follows:—

1911	\$ 1 534 537.—
1910	" 1 214 792.—
1909	" 1 425 613.—
1908	" 1 120 396.—
1907	" 1 250 855.—

The imports of the last three years were distributed as follows among the various countries of production:—

Country of origin	1909	1910	1911
	\$	\$	\$
Austria-Hungary	2 836.—	5 283.—	3 790.—
Belgium	1 313.—	856.—	2 164.—
France	1 265 975.—	1 044 306.—	1 353 036.—
Germany	60 847.—	73 553.—	58 450.—
Italy	9 151.—	7 920.—	9 090.—
Russia	730.—	3 858.—	2 101.—
United Kingdom	66 133.—	56 593.—	82 243.—
Cuba	1 575.—	2 038.—	832.—
Japan	14 065.—	15 967.—	18 539.—
All other countries	2 988.—	4 418.—	4 292.—
Total	1 425 613.—	1 214 792.—	1 534 537.—

The exports of United States' manufactures in the same department of industry were as follows:—

1911	\$ 1 009 359.—
1910	" 824 460.—
1909	" 683 253.—
1908	" 620 230.—
1907	" 604 822.—

The steady progress made, as well as the rising exports, are clearly shown by these figures, in spite of the fact that the imports still exceed the exports to a considerable extent.

The principal customer of United States' perfumery in 1911 was

Canada	with \$ 203 648.—
After her came: The Philippines	" " 40 896.—
Panama	" " 37 410.—
Australia and Tasmania	" " 31 774.—
Cuba	" " 31 624.—
Mexico	" " 22 496.—
Jamaica	" " 15 483.—
Canary Islands	" " 12 251.—
Honduras	" " 11 510.—
Nicaragua	" " 11 398.—
Egypt	" " 11 202.—

In Canada also business has been very satisfactory and the efforts of our New York branch to gain faithful customers for our manufactures in that country have been attended with gratifying success. The share of Germany in the Canadian imports in the financial year 1911/12 (up to February 29th, 1912) amounted to 11 million dollars, as compared with 10 million dollars in the year 1910/11.

Unfortunately, business with Mexico is still suffering from the notorious insecurity of the internal conditions of that country, and although it is certain that the state of affairs is slowly improving, a considerable time must elapse before the wounds inflicted by the revolution are healed. The revolutionaries possess neither money nor credit, or even sufficient ammunition, and since they abandoned the task of meeting the Government troops in the open field their cause is generally regarded as practically lost. The guerilla-warfare projected by Orozco is certain to provoke a want of discipline and discontent in the ranks of the fanatics, whose fate should then be sealed quickly. After the last two fights Argumedo and Murillo still disposed of a force of about 1500 men, but it is thought that since then many have deserted their leaders owing to lack of provisions and ammunition. On the West Coast a few small bands have been dispersed by the Government troops; in the South alone the Zapatists are still making mischief, but these, too, are being pursued energetically. The consequences of the revolution are clearly expressed in the unfavourable

Essential Oils: Imports into and Exports from the United States in the first six months of 1912 and 1911 respectively.

Imports				Exports			
		1912	1911			1912	1911
		\$	\$			\$	\$
January	Duty-free	256 390	151 617	January	Peppermint Oil	43 009	26 858
	Dutiable	103 850	68 315		Other indigenous oils	20 121	34 908
February	Duty-free	252 544	181 909	February	Foreign oils, duty-free	3 018	936
	Dutiable	71 130	94 905		" " dutiable	2 313	1 358
March	Duty-free	398 408	234 644	March	Peppermint Oil	17 069	18 396
	Dutiable	103 541	91 308		Other indigenous oils	23 481	50 532
April	Duty-free	311 456	146 147	April	Foreign oils, duty-free	2 683	3 273
	Dutiable	85 718	68 704		" " dutiable	3 019	990
May	Duty-free	206 806	195 620	May	Peppermint Oil	16 998	8 666
	Dutiable	91 264	65 498		Other indigenous oils	26 256	36 973
June	Duty-free	177 518	90 963	June	Foreign oils, duty-free	4 026	4 617
	Dutiable	92 202	45 109		" " dutiable	3 817	2 079
					Peppermint Oil	22 106	10 435
					Other indigenous oils	20 656	23 249
					Foreign oils, duty-free	1 701	2 988
					" " dutiable	4 730	4 676
					Peppermint Oil	24 061	4 044
					Other indigenous oils	46 057	22 127
					Foreign oils, duty-free	3 736	6 577
					" " dutiable	2 658	3 739
					Peppermint Oil	17 228	7 218
					Other indigenous oils	25 663	23 459
					Foreign oils, duty-free	2 308	9 138
					" " dutiable	4 933	6 198

Total value of Imports in the 1st half of 1912 \$ 2 150 827

 " " " " " " 1st " " 1911 " 1 434 739

Total value of Exports in the 1st half of 1912 \$ 341 647

 " " " " " " 1st " " 1911 " 313 434

financial condition of Mexico, both as regards the Federal Government and the separate States. According to information supplied by the Ministry of Finance the Customs receipts in the fiscal year 1911/12 have fallen short of those of the year 1910/11 by 5 million pesos, and the receipts from the Stamp Tax by 400 000 pesos. Although these figures have no very great significance in the face of the reserve funds at the disposal of the Government, thanks to the careful management of the ex-President Porfirio Diaz, it is to be feared that the falling-off will grow much greater still unless internal peace is very soon restored in the country. A law has recently been passed, and came into force on September 1st, by which the import duties are increased by 5 p. c. Furthermore, the tax on alcoholic beverages, such as beer, wine and liqueurs, has been increased by 15 p. c. *ad valorem*.

Among the South American countries in which our productions are consumed, Brazil continues to occupy the foremost place, and albeit that the economic conditions are not equally favourable in all parts of the enormous country, yet on the whole our exports have again taken a very considerable step forward. In a report of the Austrian Consul-General at Rio de Janeiro the following passage occurs: "the present economic condition of Brazil, the purchasing power of the population and the opportunities for selling goods do not present a uniform aspect yet. There is no doubt that the conditions in the coffee-growing districts, that is to say in the first place the State of São-Paulo, and in part also Minas Geraes, Espírito Santo and Rio de Janeiro, are favourable, and will probably remain so for a considerable time. These States should be energetically worked by our exporters, representatives and commercial travellers. But in the North, where the rubber-lands are, caution is to be recommended until the conditions have returned to the normal of their own accord, or have been brought back to that point by the economic measures which are about to be carried out by the Federal Government, such as the cheapening of the cost of living, the lowering of wages, the encouragement of the manufacture of rubber-goods, colonisation, the construction of railways and so on". The decrease in Brazilian exports, which manifested itself in the first quarter of the year 1911, has been made good in the course of the remainder of the year, with the result that the value of the exports for 1911 exceeds that of the imports by about £ 14 millions, a difference, however, which is less than that of the preceding year by about £ 1 million notwithstanding that the value of the exports in 1911 exceeded that of 1910 by over £ 3½ million. The favourable course which was taken by the coffee-quotations in the first quarter of 1911 has continued until nearly the end of the year, with the result that the value of the coffee exported in 1911 exceeds that of the previous year's exports by over 221 millions milreis, although the exports have only increased in bulk from 9,7 to 11,2 million bags. But on the other hand the decline in rubber-exports has also been continuous, the value of the shipments of this staple having fallen behind those of the preceding year by over 150,5 million milreis.

We give the above particulars in completion of our statements of April last.

It is gratifying to note that the Brazilian Government has rejected at any rate for the present year, the request of the United States for preferential customs duties upon a further series of goods imported into Brazil, or alternatively for an increase in the preferential treatment already accorded to United States imports into Brazil to 40 p.c. of the duty. Such a preference would, however, be of small importance so far as our manufactures are concerned, because the United States only plays a modest

¹⁾ *Handelsmuseum* 1912, 29, 414.

part as a producer of essential oils and odoriferous products. According to particulars furnished by the German Consul General in Rio de Janeiro the total foreign trade of Brazil represented the following values: — imports in 1911, £ 52798016; in 1910, £ 47871974; exports in 1911, £ 66838892; 1910 £ 63091547.

In the Argentine our turnover has continued to be satisfactory. In this important consuming market buyers are constantly showing increased appreciation of the worth of unimpeachable quality, and this fact, we are glad to note, finds expression in the healthy growth of our exports to this market, which possesses a considerable purchasing power. Unfortunately we learn from a report of the German Consulate-General in Buenos Ayres that during the first half of the present year the country has suffered economically through the outbreak of a strike among the dock-labourers in that city at a time when the corn was being threshed, which resulted in the shipment of corn being delayed from the beginning of January to the middle of February. Before this dispute was concluded, the engine-drivers and stokers came out on strike, and for about six weeks the carriage of the harvest by rail was more or less paralysed. Finally came the colliers' strike in Britain, which caused a great rise in the price of coal and a scarcity of that commodity in the Argentine and also had the effect of creating a want of sufficient tonnage.

The immediate consequences of these events for the Argentine corn harvest were a delay in the threshing operations of from 20 to 25 days, an accumulation of cereals in the various ports, owing to the impossibility of shipping them, a glut of harvest-produce in the farms, in the railway-sheds and in private warehouses throughout the country, brought about by the stoppage of railway-traffic, a considerable increase in ocean-freights from want of shipping accommodation, financial embarrassment of the farmers towards the traders and of the traders towards the banks and restriction of bankers' credits.

It was not until the beginning of April that the situation began to improve.

Considering these untoward conditions the first half-year of 1912 has come to a not unsatisfactory close.

The exports of cereals have been as follows: —

	estimate for 1912 t	shipments in the first 6 months of 1912 t	1911 t	1910 t
Wheat	3 000 000	1 840 000	1 730 000	1 230 000
Maize	5 000 000	1 100 000	130 000	400 000
Linseed	500 000	330 000	270 000	520 000
Oats	850 000	730 000	440 000	260 000
Total		4 000 000	2 570 000	2 410 000

It is a matter for congratulation that the tension between the Argentine and Italy which resulted from the application by the Argentine Government

of more stringent sanitary measures in dealing with Italian immigrants have been removed, after lasting for a year, by a sanitary convention which takes into account the rights of both countries. The Republic, which has suffered severely from the lack of Italian labour, will now be in a position to secure such labour in time for the new harvest. Argentina has now been able to form a true estimate of the high value of Italian immigration which ranks as one of the principal factors of the development and wealth of her territories, and to recognise that the cultivation of friendly relations with a nation which is able to supply labourers in such numbers and of such useful calibre is of the highest possible importance.

The most recently published annual statistics of Argentina reveal the extent to which German exports to that country have increased within recent years. According to these statistics the value of imports (in millions of pesos) from the leading foreign countries was as follows:—

	1909	1910
from the United Kingdom . . .	99,20	109,38
„ Germany	44,56	61,13
„ the United States	43,07	48,42
„ France	30,80	33,65
„ Italy	26,87	31,78

It will be seen from the above that the increase of imports from Germany (16,57 million pesos) has been far greater than that from any other country. Within the last thirty years Germany has mounted in the scale of importers into Argentine from the fifth to the second place, whereas France has receded from the second place to the fourth. Further, whereas in German exports to South America the Argentine so recently as 1895 occupied the third place, ranking behind Brazil and Chile, she now holds unchallenged the premier position.

In Chile business in our manufactures increases perceptibly year by year. In this country, which imports heavy quantities of merchandise, local manufactures in the soap- and perfumery-branches are constantly acquiring greater importance, although very considerable quantities of European manufactured goods are still marketed. The development of the local industry is worthy of special recognition when the difficulties which confront the manufacturers there are taken into consideration, inasmuch as practically all the raw materials required by the Chilean industry have to be brought from Europe. This year, moreover, an altogether unforeseen event, namely the interruption of the land-route over the Andes, has rendered business still more difficult. On this occasion it became evident that the Transandine railway is absolutely unequal to its duties and claims. For a month and a half, as a result of snow-drifts, Chile remained without any postal communication from Europe. High hopes are now entertained of the impending opening of the Panama Canal, which is to bring Chile a little nearer to the Old World. As a result of

this approximation, and in the well-founded recognition that for the further progress of the country and facilitation of intercourse, a safe port is a prime necessity, the long-projected building of a harbour at Valparaiso has at last been taken in hand. The execution of this gigantic project, which will swallow up many millions of money, has been entrusted to the well-known firm of Pearson in London, the name of which is a sure guarantee of the creation of a really practical and broadly-planned work. The rate of exchange has lately been remarkably stable and will presumably remain firm unless politics, which have already wrought so much injury to the country, should again bring forth results calculated to shatter public confidence. This was within a hair's breadth of happening last May, when the Government was again projecting the issue of 30 million dollars of paper-money, a scheme which was fortunately not carried out. In the meantime there is a constant succession of ministerial changes, and the country, which requires a strong and energetic personality at the head of affairs, is being ruled by a President who, in the opinion of his own countrymen, shows little interest in progress and generally tries to effect economies in the wrong place.

As a result of unsatisfactory harvests in 1910 and 1911 Japan has suffered this year from quite abnormally high prices of food-stuffs. Rice in particular, the principal food of the people, reached a price never before known, and still remains so dear as to affect very seriously the purchasing power of the nation. It must be admitted that the Government, by reducing the duty upon imported rice and by a rigid control of the rice-exchanges, has made energetic attempts to bring the prices down. Its success, however, has been slight, and numerous classes of the population are in a distressed condition. This precarious state of affairs, however, has been alleviated by the fact that most fortunately the crops this year are likely to be excellent all along the line. It is true that the most important crop of all, rice, is not yet safely garnered, but a bountiful result is, so to speak, already casting its shadow. The importance of this crop for the whole economic life of the country is shown, for example, by the fact that Japan has been compelled, in the first seven months of this year, to import from 25 to 30 million yen's worth of foreign rice, a figure which, of course, is much less in years of good harvests. The silk-crop is likewise satisfactory this year, and the mining-industry, being an important producer of copper, is profiting by the high prices of that metal in the world's markets.

Although Japanese industry, in some of its branches, has gained greatly as a result of the new protective tariff, its home-market has naturally been restricted owing to the dearth, and the export of its products to China, its principal foreign outlet, has suffered in consequence of the disorders in that country. This is also the reason why the Japanese imports of those articles which are of particular interest to us, have shown

a reduction. For it is a fact that what has adversely affected those imports has not only been the increased duties and the higher prices of raw materials, but still more the diminished purchasing power of the people and the lessening of sales in China, to which country many articles of perfumery are exported. The Japanese soap-industry, favoured by the protective tariff, has made notable strides of late. According to a communication by the Chamber of Commerce in Yokohama the value of its output in recent years has been as follows:—

1906	2 760 000 Yen
1907	3 180 000 „
1908	3 410 000 „
1909	3 830 000 „
1910	4 190 000 „ .

For the rest, the general commercial position is not unfavourable. It is particularly worthy of remark that the bringing into force of the new duties last summer has been carried out without any considerable disturbance in business circles, which shows that on this occasion people have not allowed themselves to be carried away by wild speculation. As a matter of fact, the imports of European goods have not been reduced to such an extent as it was originally feared they would be. And as it is to be expected that the unfavourable factors to which reference has been made above will disappear before very long, it is possible to look to the future with some degree of confidence. But the prospect of a reduction of the oppressive burden of taxation, which is the most serious obstacle to the more rapid development of the country, unfortunately remains very far distant.

The total value of the foreign trade of Japan in the first six months of 1912 amounted to 578 625 500 yen, of which 229 191 000 yen represented exports, and 349 434 000 yen represented imports, the excess of imports over exports being thus 120 243 000 yen. As compared with the same period of 1911 the exports show an increase of 24 438 000 yen and the imports of 40 595 000 yen.

The *Ostasiatischer Lloyd* publishes an interesting article on the effects of the customs tariff in Japan. "Exactly a year ago", it is there stated, "the new Japanese Customs Tariff came into force, and it may be owing to the shortness of this period that so far there is no consensus of opinion among the people of Japan with regard to its effects. There can be no doubt that many export articles have greatly benefited by the concessions made by foreign nations. In this regard we need only remind our readers of the reduced German import duties on Japanese habutae and similar cheap silk textiles. Further, the pronounced increases in the import duties on various foreign finished manufactures have led to the foundation of a whole series of new industries, especially in Osaka and Western Japan, which industries, protected from foreign competition by the import duties, are

now supplying the country with home-made goods. The *Jiji* recently published a report on the new industries of Western Japan which has been prepared by one of the high officials of the Ministry of Finance. According to this report the most noteworthy effects of the Tariff are to be observed in the glass-, nail-, zinc- and celluloid industries. The foundation of the Asahi glass works at Amagasaki near Osaka, of the nailworks of Kishimoto, of the galvanised zinc company at Osaka and of the celluloid works at Sakai, must be regarded as the immediate results of the Customs Tariff. The glass works mentioned above are said to produce monthly 10 000 cases, thereby already covering 20 p. c. of the annual consumption of glass in the country. As up to the present the works are said to be doing a very profitable trade indeed, and as the glass produced there is reputed to be in no wise inferior to the foreign article, a further extension of this industry appears to be desirable. The same might be said of the nail works. The new works at Kishimoto are stated to have an annual output of 6000 tons of nails, the older works (Yasuda's) of 14 000 tons, and the 20 000 tons which represent the combined output of the two works already equal two-thirds of the total quantity of nails imported from France. The establishment of the zinc refinery at Osaka has almost put an end to the practice of sending Japanese zinc ore abroad and then reimporting it in the purified state as spelter; 1200 tons, equal to two-thirds of the annual imports, can now be manufactured in Japan. The annual consumption of celluloid in Japan is estimated at about 1 000 000 lbs., and the two celluloid works at Sakai and Abosbi, taken jointly, already produce more than this quantity. Another result of the import tariff is said to be that the great English soap firm of Lever Brothers have established their own works in Western Japan".

The reports from China are a little more favourable, but some time must still elapse before the new régime can offer sufficient security for the peaceful and healthy economic development of the country. Important factors towards the realisation of this object are the prospective European loan as well as the sanction by the Government of a great national scheme for railway extension. It is also rumoured that a project is now before the Government of the Republic for throwing open the whole of China to foreign enterprise and for granting foreigners the right of domicile. These reforms would mean important progress, and German industry will be well advised to take steps in good time to secure its share of supplying the certain future requirements of this rich country, which is thus preparing to throw itself open to the world.

Commercial Notes and Scientific Information on Essential Oils.

Almond Oil, Bitter. The malpractices of which complaint has so often been made already continue to prevail in the trade in essential oil of bitter almonds. Adulteration with synthetic oil still remains a matter of daily occurrence, and we regret to say that the warnings which we have sounded so often and so emphatically in our *Reports* have so far brought very little improvement indeed. In the department of bitter almond oil free from hydrocyanic acid in particular, artificial oil is used to a truly incredible extent by certain firms, whenever they have come to the end of their power of competing fairly. Bitter almond oil is an article of confidence which should be bought by the consumers only from sources where quality is the paramount consideration, and from firms who are themselves manufacturers of the article, for only such are in a position to give a full guarantee for the goods they supply.

Some time ago we mentioned a paper by V. K. Krieble¹⁾ on amygdalin. Since that time the author has continued his investigations²⁾ and has observed that the slightest traces of hydroxyl ions racemise the amygdalin, and that the cyanide radical is necessary to effect this change. It was discovered that racemic amygdalin consists of 56,25 p. c. *d*- and 43,75 p. c. *l*-amygdalin. The circumstance that the racemic mixture, after being dried on the water-bath, shows increased rotation is due to the action of a small quantity of hydroxyl ions. These hydroxyl ions are generated by the hydrolysis of the barium salt of an as yet unknown acid which is always associated with amygdalin in minute quantities.

The author finally succeeded in resolving racemic amygdalin into its optically active constituents. In the course of hydrolysis with moderately concentrated sulphuric acid, *d*-amygdalin is broken up into glucose and *d*-mandelonitrile. With hydrochloric acid it affords glucose and *d*-mandelic acid. *d*-Amygdalin is split up by emulsin into benzaldehyde, glucose, and hydrocyanic acid. It had already been observed previously³⁾ that *l*-amygdalin behaves similarly.

Almond Oil, Pressed. See Chemical Preparations and Drugs, p. 117.

Ambrette Seed Oil. As our cheap supplies of ambrette seed are used up, we have found it necessary to raise the prices of both our qualities of ambrette seed oil to a not inconsiderable extent. For the moment suitable distilling material is only obtainable at very high prices

¹⁾ *Journ. chem. Soc.* 95 (1909), 1437; *Report* April 1910, 18.

²⁾ *Journ. Americ. chem. Soc.* 34 (1912), 716.

³⁾ *Comp. Report* October 1909, 23.

and we are therefore working up only as much as is absolutely necessary. Sooner or later the market will probably give way again, experience showing that when the prices are profitable the production is generally considerably increased. Most of the seed on offer was West Indian, Java having only sent small quantities.

On the oil-content of *gum Ammoniacum* see p. 24.

Angelica Oil. The angelica plantations here in Miltitz as well as in Thuringia are still suffering from the results of the dry summer of 1911. Young plants were everywhere wanting last spring because last year's sowings had been an unqualified failure. The dampness and the almost sunless summer of 1912 have of course also had an injurious effect and we therefore believe that we shall not go wrong if we describe the present outlook as unfavourable. Judging by the appearance of the fields, the yield of root seems hardly likely to equal one-third of a normal crop. Whether it will be possible to procure a sufficient quantity of angelica seed for distilling purposes appears to be doubtful, as the entire production is certain to be required for sowing purposes.

Anise Oil, Russian. The present year's harvest of Russian anise has suffered a few weeks' delay, and we are therefore, to our regret, unable on this occasion to express a definite opinion as to its result. The information which has reached us from various quarters up to the time when the present *Report* was written agrees in describing the probable yield this year as considerably in excess of that of 1911. According to the statement of one of our authorities, the area under cultivation is less by 1000 dessiatines this year than last, but from another quarter it is asserted that it is, if anything, rather larger than in 1911. At the first fair in Krasnoie only very small quantities were brought to market, which were bought up at noticeably higher prices than those of 1911. It would appear that the paucity of the supply at this fair was mainly caused by the delay in getting in the crop. The new seed is of good appearance; it is small and green in colour and for this reason a brisk export-demand is expected. Whether this year's quality is also suitable for distilling purposes, that is to say whether its oil-content is satisfactory, cannot as yet be stated. It will therefore be necessary to await the further development of events before it is possible to form an idea of the probable course of prices of Russian anise oil. From an authoritative source the total yield of the crop is estimated at about 250 car-loads.

Arnica Oils. A fresh supply of arnica flower oil is again in stock. In many parts the damp weather which prevailed during the summer-months has impeded the collection of the flowers.

We have also at length been able again to distil a quantity of oil from arnica root, although the high price of the raw material cannot be

said to hold out any inducement to buy. Owing to the drought of last year the development of the roots had suffered greatly, and we have found ourselves compelled to list the new distillate at an increased price, notwithstanding which our profit on this oil is very moderate.

Asafoetida Oil. In our last *Report*, p. 28 we commented upon the interesting study on *Asa foetida* by Harrison and Self. Since then the same authors have examined a further series of asafoetida samples¹). A few of these contained heavy admixtures of gypsum. The characters recorded for the oils distilled from the, in part unadulterated, samples are set forth in table form. The oil-yield ranged from 4,6 to 19,6 p. c. : d 0,918 to 0,993, $\alpha_D - 11^\circ 43'$ to $+ 10^\circ 58'$, $n_{D20} 1,4951$ to $1,5259$; percentage of sulphur in the oil 8,9 to 31,4.

Ammoniacum, galbanum, and elemi being known adulterants of asafoetida, Harrison and Self have distilled the oils from these resins. The oil-yield of ammoniacum was 0,08 to 0,20 p. c., hence the addition of this gum-resin to asafoetida would lower the oil-yield of the product. But as the oil-content of unadulterated asafoetida varies, the determination of the oil-yield is of little value in the evaluation of asafoetida. Two samples of galbanum yielded respectively 10,3 and 11,4 p. c. of oil : d 0,908 and 0,955, $\alpha_D + 15^\circ 14'$ and $+ 7^\circ 30'$, $n_{D20} 1,4856$ and $1,4863$. A sample of elemi yielded 9,6 p. c. oil : d 0,904, $\alpha_D + 38^\circ 22'$, $n_{D20} 1,4869$.

Oil of *Backhousia citriodora*, see Citral under Chemical Preparations and Drugs.

Oil of Sweet Basil. This oil, which several years ago was so greatly in request, has remained very neglected throughout the summer, and our experience that this article is by no means so popular in the perfumery- and soap-industries now as it used to be has again been confirmed during the past few months. But as no parcels of importance have come to hand, either from Java or from Réunion, the price has been maintained at the old level.

The article on the essential oils of the different varieties of *Basilicum*, which appeared in the *Berichte* of Roure-Bertrand Fils (October 1910, 38; comp. *Report* April 1911, 22) has recently been published by G. Laloue in the *Bulletin de la Société chimique* [IV. 11 (1912), 491].

Bay Oil continues to be very scarce indeed and at times we only succeeded through the assistance of our New York branch in procuring a sufficient supply. Moreover, the quality very often left something to be desired; and it is therefore a source of increasing regret for us that owing to the lack of leaves suitable for shipment to Europe we still remain dependent upon the West-Indian distillates. All our efforts to procure

¹) *Pharmaceutical Journ.* 89 (1912), 139; *Chemist and Druggist* 81 (1912), 202, 204.

distilling-material have failed so far. The imperfections of the imported oils appear in most cases to be the result of primitive distilling-plants, or only in sporadic cases could deliberate adulteration be detected. At times the demand was not particularly brisk, but the bulk of our imports has been used for the preparation of our terpeneless bay oil, which has enjoyed an increasing popularity in spite of its high price.

The experiments in the cultivation of the bay tree (*Pimenta acris*, Kostel.; N. O. Myrtaceæ) which have been carried out at Montserrat have been attended with a fair measure of success¹). In the year 1908, 850 year-old seedlings per acre were planted at distances of 6 feet, in rows 9 feet apart, cotton being selected to fill the spaces between the rows of seedlings. The first crop of leaves was gathered in June 1911, when the shrubs were 6 feet high. From 100 lbs. leaves 16 oz. (= 1 p. c.) oil was obtained. The bay-shrub has also been planted in another part of the island. Each year the yield of leaves per acre has shown an increase: in 1905 it was 2660 lb., and in 1910 8844 lb., representing 425 and 1414 oz. oil respectively.

Birch Bud Oil. The manufacture of birch oil hair-washes, &c., as yet shows no signs of diminution, and our oil has therefore enjoyed a continued sustained demand. Raw material has lately been sparingly offered, and for this reason we regard it as not improbable that the price of oil will advance in the near future.

Buchu Leaf Oil. We have at last succeeded in acquiring a small parcel of pure oil with a normal content of buchu camphor, but as this parcel only amounts to a few kilos we must continue to describe the article as unchanged and firm. Suitable raw material is still wanting and as yet it is therefore impossible to manufacture buchu leaf oil on the scale of former years.

Cajuput Oil. During the summer-months the state of the market has been very quiet. Although supplies did not arrive very plentifully, the demand was on the whole stagnant, and this condition of things is so chronic that we came to the conclusion several years ago that the use of cajuput oil is declining more and more. That in the producing districts also cajuput has lost much of its importance is evident from the mere fact that for some time it has ceased to be enumerated in the official list of exports from Macassar.

Calamus Oil. As there has been no lack of excellent raw material at advantageous prices, this oil has continued to be available at low rates. No alterations in price are to be recorded.

¹) Report of the Botanic Station, Montserrat 1910—1911, p. 16. Quoted from *Bull. Imp. Inst.* 10 (1912), 147.

Camphor Oil. No price-fluctuations of any particular importance have occurred during the last few months in the camphor oil market. The Japanese have stood firm in their quotations for crude oil, and the American buyers interested in the article have shown greater readiness to concede these demands than has been manifested in European consuming circles where considerable stocks were still available. The producers have continued to display an astonishing dexterity in so adapting their offers to the demand as to maintain the firmness of the market. The enquiry for both our light and our heavy camphor oil has remained brisk throughout so that we had no difficulty in disposing of our considerable output at steady prices. In spite of the receding movement in the turpentine oil market, the consumption of light camphor oil has been well maintained irrespective of the fact that its principal use is in the manufacture of cheap turpentine substitutes.

A report issued by the German Consulate of Nagasaki contains a review of the production of camphor and camphor oil in Formosa and Japan¹⁾ from which we abstract the following particulars:—

Production of camphor and camphor oil

(in 1000 piculs²⁾).

<i>Formosa</i>					<i>Old Japan</i>						
1907	1908	1909	1910	1911	1907	1908	1909	1910	1911		
Camphor . .	35	35	35	53	45	Camphor . .	7	8	8	10	11
Camphor oil	41	44	38	58	56	Camphor oil	9	10	11	16	18

Almost the whole of the camphor prepared in Formosa is shipped to foreign countries, only small quantities being sent to Japan.

The exports from Formosa to foreign countries are detailed in the following statistics:—

Shipments to foreign countries (in piculs).

<i>Country of destination</i>		<i>Camphor.</i>				
		1907	1908	1909	1910	1911
Hong Kong		14 287	4 212	—	—	—
British India		—	30	1 422	1 870	945
United Kingdom		4 110	3 450	5 680	4 068	3 540
France		—	2 090	10 119	6 815	4 217
Germany		—	400	18 496	13 560	17 810
Austria		—	—	—	—	250
U. S. America		4 251	6 528	14 313	22 071	15 296
Total		22 648	16 710	50 030	48 384	42 058

¹⁾ *Nachrichten f. Handel u. Industrie* 1912, No. 73, p. 6.

²⁾ A picul equals 60 kilos.

Exports to Japan.

	1907	1908	1909	1910	1911
Camphor	8 261	4 025	—	263	45
Camphor oil	41 950	45 193	36 394	58 766	52 008

From Old Japan the following quantities were exported: —

Camphor.

Country of destination	1907	1908	1909	1910	1911
Hong Kong	128	266	996	131	308
British India	4 173	2 644	4 870	4 529	5 707
Straits Settlements	91	94	33	50	81
United Kingdom	867	1 288	10 617	6 578	6 577
France	4 002	2 487	6 169	8 725	7 959
Germany	7 387	3 180	6 390	3 570	5 203
U. S. America	13 277	7 221	10 081	7 895	7 037
Canada	30	19	83	121	116
Australia	541	514	441	636	943
Total, including countries not enumerated	30 577	18 075	40 505	32 751	34 410

Camphor oil.

Country of destination	1907	1908	1909	1910	1911
United Kingdom	2 148	434	387	3 850	—
France	849	580	108	231	—
Germany	8 280	3 962	1 402	4 732	—
Italy	1 878	1 664	2 036	600	—
U. S. America	5 477	5 900	8 714	7 257	—
Total, including countries not enumerated	18 706	12 600	12 728	16 869	17 417

Between the years 1907 and 1910 inclusive the total exports of crude camphor¹⁾ from China reached the figures reproduced in the table below:

Year	Total exports		Sent to	
	Piculs	Value in Hankwan taels	Shanghai	Amoy and Foochow
1907	25 789	2 077 475	4 647	19 711
1908	13 072	850 135	4 064	8 257
1909	9 759	680 827	4 889	3 945
1910	5 597	391 100	4 410	1 005

Whereas the camphor exports from Fukien in the year 1907 amounted to 19 711 piculs (1 191 500 kilos), they have lately fallen steadily to 576 piculs

¹⁾ Chem. Zeitschr. 11 (1912), 106.

(34 821 kilos) in the year 1911. Of this quantity 559 piculs (60 453 kilos) were shipped from the port of Foochow and 17 piculs from that of Amoy. The destination of the whole of the exports was Hong Kong¹⁾.

Numerous enquiries on the part of planters have induced the Government of the Federated Malay States to publish a treatise by B. J. Eaton²⁾ on the cultivation and preparation of camphor. The author describes the different varieties of camphor, including ordinary camphor from *Cinnamomum Camphora*, Borneo camphor from *Dryobalanops aromatica* and Ngai camphor from *Blumea balsamifera*. He next deals with the geographical distribution of the camphor tree and its cultivation in foreign countries and gives a few statistical data on the exports of camphor from China and Japan.

The first experiments in the cultivation of the camphor tree in the Malay States were made in the year 1904 at Batu-Tiga, Selangor, seeds having been obtained from Yokohama for the purpose. The plants flourished excellently and in 1909 the first camphor was distilled. The raw material consisted of shoots from 5 year old trees and the result of the experiments is shown below: —

Material	Yield calc. based upon original material
Cut leaves	1,17 to 1,22 p. c.
Small stems	0,06 „ 0,45 „
Mouldy leaves	1,25 „ 1,47 „
Leaves and stems	1,25 „ 1,58 „
Air-dried leaves	1,10 „ 1,16 „
„ mouldy leaves	1,54 p. c.

In each case the distillate consisted of camphor with very little oil.

These experiments were repeated upon a large scale with a large distilling apparatus. The raw material consisted of the parts of an entire 5 year old tree.

Material	Yield p. c.
Leaves	1,00
Stems under 1/2 inch diameter	0,22
Woody stems over 1/2 inch diameter	0,61
Roots	1,10

The distillates consisted principally of camphor; the roots alone yielded an oil, which possessed an odour reminding at the same time of camphor and of lemons. Afterwards numerous experiments were carried out with various distilling apparatus which had been partly modified. All these

¹⁾ Nachrichten f. Handel u. Industrie 1912, No. 63, p. 3.

²⁾ Camphor from *Cinnamomum Camphora* (The Japanese camphor tree), cultivation and preparation in the Federated Malay States. Department of Agriculture. Bulletin No. 15. February 1912.

experiments are described in detail by Eaton, who also gives several illustrations of the distilling plant.

Finally, the author gives a review of similar experiments in other countries, the results of which are shown in the subjoined table: —

in	Distilled by	Yield p. c.	Material	Properties of the Distillate
Ceylon	Willis and Bamber	1	Leaves and small stems	—
India	Hooper	1	—	{ Contained from 10 to 75 p. c. camphor.
German } E. Africa }	Lommel	{ 0,06 to 0,1 0,22	Branches and thin twigs Young shoots	{ Camphor and oil.
Jamaica	Duncan	0,61 0,05 2,37 2,52 1,39	Wood Twigs Green leaves Dried leaves Dead leaves	{ Crude camphor.
West Indies . .	Watts and Tempany	0,5 0,5 0,7	Wood Leaves and twigs ¹⁾ Leaves and twigs	{ Camphor and oil.
Italy	Giglioli	1,2 to 1,5 2,4 to 3,0 0,02 to 0,25	Green leaves Dry leaves Twigs	{ Camphor.
America	Hood and True . .	2 0,7 2,77	Shed leaves Trees from shady places Trees from sterile, shady places	{ Camphor and oil.

We mentioned recently²⁾ an article by Lommel on the distillation of camphor leaves at Amani. Since that time, as we observe from a communication by A. W. K. de Jong³⁾, camphor leaves have also been distilled in Java. From 3560 kilos green (?) leaves, de Jong obtained 31,15 kilos camphor and 14,1 litres oil. 376 kilos branches (probably without leaves) only yielded a trace of oil. De Jong distilled with steam of 3 to 5 atm. The steam was passed through a galvanised iron case, enclosing three cylindrical cooling vessels filled with water, the floor and walls of the case being also washed by cooling-water. In the floor of the case was a cock for drawing off the water of condensation. When the distillation was concluded the cooling vessels were removed from the case and the camphor which had distilled out was collected.

Cananga Oil. According to reports to hand from Java, the native producers have now considerably raised their limits and in the meantime

¹⁾ The small yield is explained by insufficient cooling.

²⁾ Report April 1912, 35.

³⁾ *Teysmannia* 1912, No. 2, p. 125. From a reprint kindly sent to us.

the upward movement in prices which had been foreseen has become fact. This movement has already made itself felt in Europe and America, where, owing to the very lively demand, the upward tendency has found additional support. Consumers who have followed our advice and have covered their requirements for the near future at the old prices will have no cause for regret, for all the signs point to further advance in value for some considerable time ahead. So far as quality is concerned great caution is advisable in buying, because it is difficult to examine the supplies in the producing centres, and in view of the increased value of the oil the natives are particularly interested in increasing their output. It stands to reason, of course, that they will not be particularly scrupulous in the ways and means adopted to achieve this end. As already mentioned on a previous occasion, we have taken special measures to cover our considerable requirements, and we are at any time in a position to offer our customers the finest quality at the best possible prices.

Caraway Oil. We will begin our report by bringing up to date the statistics relating to the production which are published annually by the Dutch Ministry of Agriculture. According to this authority the result of the crop has been as follows:—

	1911	224 419	bales of 50 kilos each,
compared with {	1910	179 812	" "
	1909	171 447	" "

The increase of the area under caraway during the past 3 years is shown by the following table:—

Province	1909 Hectares	1910 Hectares	1911 Hectares
Groningen	2024	2696	3329
Friesland	50	68	62
Utrecht	10	5	9
North-Holland	2806	2517	2440
South-Holland	276	252	252
Zealand	1131	1291	1268
North-Brabant	817	864	870
	7114	7693	8230

The average yield per hectare was as follows:—

1911	27,3	bales
1910	23,3	"
1909	24,1	"

We have already previously expressed the view, which is confirmed by the above figures, that the crop of 1911 has constituted a record.

Shortly after the publication of our April *Report* the first official communication on the crop-prospects issued by the authority named made its appearance. It indicated that the result in the present year was likely to be unfavourable. The dry summer of 1911, the communication in question states, was very unfavourable for the development of the young caraway-plants. When the winter-cover was removed the fields were found to be in such a condition that the greater part had to be ploughed up. As a result there is now very little land under caraway in all the principal districts, such as Groningen, North- and South-Holland, Zealand, and the western part of North-Brabant. The National Instructor in Agriculture for Western North-Brabant, for instance, reported that in his district the caraway-plantations only cover from 10 to 20 p. c. of the area they occupied in 1911. The plants had moreover developed very badly. In Groningen the condition of the fields was moderate to fairly good; in North-Holland fair on clay-soil and fairly good on peat-soil, in South-Holland and Zealand moderate and in North-Brabant rather bad.

It is easy to understand that as a result of this unfavourable outlook the caraway market immediately began to assume a much firmer tone, although the heavy stocks still remaining over from the year 1911 prevented the prices from advancing beyond a certain limit. Naturally, the price of caraway oil followed the seed-market. Another official report appeared under date of July 15th, from which it appeared that the area under caraway this year amounts to 3266 hectares only, compared with 8230 hectares in 1911 (see above), and that therefore the crop will be a very small one. The news from the various districts is as follows:—

Zealand, bad; North-Holland and North-Brabant, rather bad; Groningen rather bad to moderate; South-Holland, moderate. Only from Friesland, where but very little is grown, the report is fairly good.

In the meantime the total yield has also been made known. It amounts to 25 000 bales only, that is to say, to little more than one-tenth of last year's crop. With such a pitiable result no doubt will be entertained that the increase in price which we have been forced to declare for all varieties of caraway oil is thoroughly justified, or that as soon as the stock of last year's seed is approaching exhaustion it will probably be necessary to announce a fresh advance.

An official report on the condition of the young caraway plants dated September 12th is as follows:—

In Groningen a few fields will have to be ploughed up and in North Brabant the plants are generally too weak. In North-Holland and in Western North-Brabant the condition is fairly good, elsewhere it is good.

Cardamom Oil. In spite of the high values of the raw material (for Malabar cardamoms suitable for distillation about 750 *M* per 100 kilos

must now be paid), we have been compelled to work up considerable parcels in the course of the summer on account of the exceptional demand which set in from the United States. We have been under the necessity to raise the price of our distillate on several occasions, but this has not adversely affected the extent of the demand. A few samples of "cheap" cardamom oil were shown on examination in our laboratory to be heavily adulterated, the most surprising sophistication of all having been practised in England, where a camphor oil preparation which had turned out a failure was offered under the name of cardamom oil.

The cultivation of cardamoms, to which we have briefly referred on a previous occasion¹⁾ is described in detail in a British journal²⁾.

The cardamoms of British commerce are all derived from *Elettaria Cardamomum*, Maton³⁾, N. O. Zingiberaceæ, which grows wild or is cultivated on the Malabar coast and in Ceylon. There is a large market for the spice in Calcutta; the annual consumption in India and Burma is computed to be nearly 1 000 000 lbs. Formerly scarcely any other than Malabar cardamoms were imported into Britain, but the Mysore variety now affords most of the fine quality. The latter plant possesses a more robust habit and bears exposure better than the Malabar type. It is not known how the district name "Mysore" came to designate the variety of a cardamom plant. There appear to be two varieties of Malabar plants, var. *minus* being confined to Southern India and var. *majus* growing in Ceylon. The latter is distinguished by its shorter stems, broader leaves and less globose fruit. In the shady mountain forests of Canara, Cochin and Travancore the cardamom plant grows between the altitude of 2500 and 5000 feet. The plant is best suited to a rich, moist, loamy soil protected from strong winds. These conditions are met with in the betel nut and pepper gardens of Mysore and of Canara, and also in the cultivated cardamom valleys of Ceylon.

In the forest-district of Coorg (Mysore) the cardamom gardens are laid out in February or March, simply by making clearings in the forest, a space of some 20 to 30 yards of jungle being left between the gardens. Superstition plays an important part, felling of the trees only permissible on certain days of the week and before noon. The natives also believe that the presence of such plants as ebony, nutmeg, and pepper favourably affects the development of the cardamom plants. In the fifth year a full crop is produced. After seven years more the plants become sickly. Some of the large trees in the jungle-screen surrounding the fields are

¹⁾ Report April 1910, 29.

²⁾ Chemist and Druggist 80 (1912), 367.

³⁾ Comp. Report October 1910, 32.

elled; the falling trunks kill many of the cardamom stems, thus stimulating the rhizomes to produce new shoots, thereby renewing the producing capacity of the plot for another eight years, when the process of renovation is repeated.

In Ceylon the cultivation is carried out much more systematically. The favourite cardamom districts are Matale, Medamahanwara, and Hewa-nata. The undergrowth of the land intended for a cardamom-plantation is cleared; holes are dug, $1\frac{1}{2}$ to 2 feet wide, 12 in. to 15 in. deep and 7 feet apart in rows at a similar distance. The bulbs must not be planted too deep or they will rot. The use of seedlings instead of bulbs is increasing, however, the Mysore variety being most frequently grown from seed. Curiously enough, only a small proportion of the seed germinates.

In Ceylon the plants flower almost all the year round; picking begins at the end of August and continues until April. The fruit is carefully dried by exposure to the sun or in wet weather by artificial heat. Machines for removing the calyx tube and the stalk have been introduced and after passing through these the capsules are graded and treated with sulphur-vapour.

The table below shows the exports for the past ten years.

Exports from Ceylon.

Year	Acreage planted	Export in lbs.	Year	Acreage planted	Export in lbs.
1901	8621	559 704	1907	8451	789 495
1902	9746	615 922	1908	8350	715 418
1903	9500	909 418	1909	7738	824 008
1904	9300	995 680	1910	7426	639 007
1905	8870	874 625	1911	7300	564 819
1906	8744	732 136			

Carrot Oil, Wild. An oil of wild carrot, which was obtained in the French Department of Puy-de-Dôme by the distillation of the entire plant¹⁾ was most probably the product of *Daucus Carota*, L. The oil gave the following constants: d_{15}^0 0,9016, α_D — $6^\circ 56'$, sap. v. after half an hour's boiling with alcoholic potash about 169, after one hour's boiling 195,4, ester v. after acet. 226,8, sol. in its own vol. of 80 p. c. alcohol. When more alcohol was added, opalescence ensued.

Cassia Oil. The movement in prices in this important article is clearly shown in the table below, which refers to 80 to 85 p. c. oil, the only quality supplied by us: —

¹⁾ *Berichte von Roure-Bertrand Fils*, April 1912, 31.

Price of Cassia Oil.

on 1 st April . . .	3/9	cif.	on 1 st July . . .	3/4 ¹ / ₂	cif.
" 15 th " . . .	3/8	"	" 15 th " . . .	3/7	"
" 1 st May . . .	3/8	"	" 1 st Aug. . . .	3/5	"
" 15 th " . . .	3/8	"	" 15 th " . . .	3/5	"
" 1 st June . . .	3/7 ¹ / ₂	"	" 1 st Sept. . . .	3/8	"
" 15 th " . . .	3/4	"	" 15 th " . . .	3/7 ¹ / ₂	"

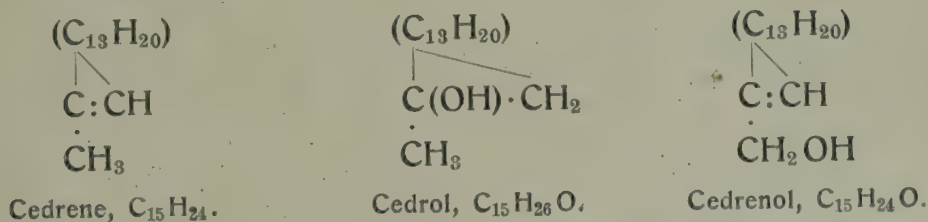
These price-fluctuations are sufficient to show the pronounced instability of the market. Quite recently a certain degree of quietness has supervened but it would appear as if only the customary autumnal increase in demand were needed to cause the prices to tighten once more. According to British Consular Report from Wuchow, the entire cassia trade is now under the control of a ring of Chinese merchants in the province of Kwangtung, who also control the exports of cassia lignea. The total value of the cassia oil exports in the year 1911 amounted to £ 28964, of which about one-half was sent out via Hong Kong. It is not stated by what route the other half was exported; we know of no other shipping-port for cassia oil than Hong Kong. It is said that in 1911 2200 cases passed through the last-named port, as compared with 1400 cases in 1910. The value of the cassia oil exported to the United States in 1911 was £ 556 as compared with £ 4880 in the previous year. On this occasion no further particulars concerning cassia oil are available.

Cedar Leaf Oil. This oil, which, as is well known, is distilled in the State of Virginia, U. S. A., has lately been employed to a considerable extent in the manufacture of soaps for veterinary purposes, as its peculiar odour is said to banish parasites. There is no difficulty in procuring large quantities of it.

Cedarwood Oil. We prepare this article on the largest scale imaginable, and we only sell oil of our own distilling, because the cheap quality with which the United States at intervals flood the European market has proved to be too inferior to answer the requirements of the perfume manufacturers. Many a soap-maker who had taken up the cheap American oil from motives of parsimony, has returned in bitter disappointment to the employment of our distillate. In our manufacture an inspissated cedarwood oil for optical purposes also plays an important part. We would, however, seize this opportunity to point out that the slight condition of turbidity which is occasionally noticeable in this oil is merely determined by temperature, and immediately disappears when the bottle containing such oil is opened and gently warmed. The turbidity cannot be prevented, but it does not affect the quality of the oil in the least.

F. W. Semmler, in conjunction with E. W. Mayer¹⁾, has continued his researches in cedarwood oil, and has discovered a new constituent in the form of a primary sesquiterpene alcohol, to which he has given the name of cedrenol. This body occurs in those fractions of the oil which boil between 152 and 170° (7 mm.) ($\alpha_{D20} + 17,5^\circ$) and can be isolated therefrom by warming with phthalic anhydride in benzene solution. The alcohol, when purified from primarily-produced acetate, possesses the following properties: b. p. 166 to 169° (9,5 mm.), $d_{20} 1,0083$, $\alpha_{D20} \pm 0^\circ$, $n_{D20} 1,5212$. The acetate occurs in the form of a colourless liquid, b. p. 165 to 169° (9,5 mm.): $d_{20} 1,0168$, $\alpha_D - 2^\circ$, $n_{D20} 1,5021$. Cedrenyl chloride boils between 150 and 165° (10 mm.): $d_{20} 1,001$. When heated with sodium and alcohol the chloride yields an ethylether and a hydrocarbon which proved to be identical with cedrene, as was shown by oxidation into cedrene keto-acid and into cedrene dicarboxylic acid²⁾.

Cedrenol stands in the same relation towards cedrene as do the two primary alcohols of the santalol series towards the sesquiterpenes $C_{15}H_{24}$, the santalenes; and as myrtenol and the gingergrass alcohol stand towards pinene and limonene³⁾. The primary CH_2OH -group in the cedrenol molecule occupies the same position which is occupied by the CH_3 -group in cedrene and in solid cedrol. Hence the relation of cedrene towards cedrol and cedrenol is as follows:—



In addition to cedrenol, Semmler and Mayer⁴⁾ have observed in cedar oil a saturated alcohol; *pseudo*-cedrol ($C_{15}H_{26}O$). This alcohol was found to occur in the fractions boiling between 145 and 155° (10 mm.), from which the cedrenol was removed by heating with phthalic anhydride. It boils between 147 and 152° and constitutes a viscous oil with the following constants: $d_{20} 0,9964$, $\alpha_{D20} + 21,5^\circ$, $n_{D20} 1,5131$. Its tertiary character is evident from the fact that when heated with zinc dust in a sealed tube to 225 to 235° its oxygen was abstracted from it, and the corresponding saturated hydrocarbon, dihydrocedrene, was formed, the latter, in this case, being contaminated with about 50 p. c. cedrene. In order to obtain dihydrocedrene in the pure state, ozone was introduced into the hydrocarbon-mixture in a chloroform-solution until bromine ceased to lose its colour. Dihydrocedrene boils between 109 and 112° (10 mm.): $d_{20} 0,907$, $\alpha_D + 37^\circ$,

¹⁾ Berl. Berichte 45 (1912), 786.

²⁾ Comp. Report April 1912, 173.

³⁾ Comp. Report April 1911, 76.

⁴⁾ Berl. Berichte 45 (1912), 1384.

n_D 1,4882. It differs in its physical properties from the dihydrocedrene which was prepared by reducing cedrene with platinum and hydrogen, the latter possessing the following constants: b. p. 122 to 123° (10 mm), $d_{20} 0,9204$, $\alpha_{D20} +2^\circ$, $n_{D20} 1,4929$. Cedrene resulted when formic acid was allowed to react upon *pseudo*-cedrol, and was identified by the preparation of the cedrene keto acid and of cedrene dicarboxylic acid.

Cedrol and *pseudo*-cedrol are chemically identical, but physically they are isomerides.

On the identity of natural and artificial cedrene, see p. 150.

Celery Oil. In the course of the summer we have several times been under the necessity of raising our prices, because celery seed was unobtainable and we are now again compelled to declare a fresh advance in order to bring our quotations in harmony with the fact that the crop of celery seed in France has once again been a failure.

Our celery oil from leaves of our own growing continues to be extremely popular, and has become practically indispensable in the manufacture of soup-seasonings, sauces, condiments and preserves.

An oil¹⁾ distilled in Algeria from wild celery-plants was found to possess the following characters: $d_{15} 0,8467$, $\alpha_D +69^\circ 18'$, acid v. sap. v. 16,7, ester v. after acet. 20,9. It gave a cloudy solution in 15 vols. 85 p. c. alcohol; dissolved with faint opalescence in 4,5 vols. 90 p. c. alcohol and gave a clear solution with any proportion of 95 p. c. alcohol.

Chamomile Oil, German. Having been successful in acquiring a few chance-parcels of distilling material of good quality, we have lately been able to make a corresponding reduction in our quotations. Whether it will be possible to maintain the present reduced price for any length of time is, however, doubtful in view of the very sustained demand for our distillate.

Chamomile Oil, Roman. As we are only able to grow Roman chamomiles on a modest scale on our Miltitz plantations, we have remained mainly dependent upon the English producing districts. In that country all the stocks were exhausted long ago and what can only be described as fancy prices had to be paid for the odds and ends which it was possible to scrape together from second-hand holders. With regard to the new crop the report goes that although the output of flowers has been rather in excess of that of 1911, the oil-yield has left somewhat to be desired and that there can be no question of any reduction in prices. There are only a few growers of chamomiles in the Mitcham district, and a considerable portion of their production was so to speak taken out of the

¹⁾ *Berichte von Roure-Bertrand Fils*, April 1912, 30.

ands while the distillation was still proceeding. Our impression is that the new crop will have no weakening effect upon the market.

Cinnamomum Oils. The *Cinnamomum* species of Australia have been described by R. T. Baker in Vol. 13 of the Australian Association for the Advancement of Science (May 1, 1912)¹). As we referred to a lecture by Baker on the same subject in our *Report* of April 1911 (p. 38) a mere reference to the publication will here suffice.

Oil of Cinnamomum glanduliferum. In our *Report* of October 1910, p. 145, we stated that R. S. Pearson had obtained from the leaves of *Cinnamomum glanduliferum*, Meissn. (N. O. Lauraceæ), known as "Nepal sassafras", or "Nepal camphor tree", a camphor which may probably be regarded as identical with the Japanese commercial product. On the other hand, according to S. S. Pickles²), the oil distilled from the wood of the plant contains none, or scarcely any, ketones. Pickles' distilling material consisted of billets of heartwood free from bark. The ground wood yielded 2,95 p. c. oil (calculation based upon the wood before grinding), or 4,16 p. c. (calculation based upon the ground wood), the difference being due to the fact that the wood had lost moisture during the process of grinding. The oil constitutes a pale yellow liquid, with a well-defined odour of safrol, with a suggestion of anise: d_{15}^{150} 1,1033, $n_{D20}^{20} - 0^{\circ} 4'$, sap. v. 2,8, ester v. after acet. 7,0, sol. in 5 vols. and more 80 p. c. and in half its vol. 90 p. c. alcohol. Terpenes, acids, alcohols, esters, aldehydes and ketones are either absent altogether or occur only in very small proportions. The principal portion of the oil boils between 245 and 280° and contains an abundance of safrol with the following constants: m. p. 9°, d_{15}^{150} 1,1059, $\alpha_D \pm 0$. It was identified by oxidation into piperonal (heliotropin), m. p. 37°, and from its α -nitrosite, m. p. 130 to 131°. In a fraction melting between 152 and 157° (12 mm.), Pickles detected myristicin, which he converted into dibromomyristicin dibromide (m. p. 129°) and dibromomyristicin (m. p. 52°). The fraction containing myristicin was heated with alcoholic potash in order to convert the allyl-group into the propylene-group, and was afterwards oxidised with potassium permanganate, when myristicinaldehyde (m. p. 130°) and myristicinic acid (m. p. 212,3°) together with trimethylgallic acid (m. p. 167 to 160°) were formed. The trimethylgallic acid points to the presence of elemicine in the fraction containing myristicine which was treated with potash. It is therefore to be assumed that elemicine is a constituent of the original oil. The other constituents of the oil are free palmitic acid (m. p. 62,5°), a phenolic body, and a mixture of the esters of the lower fatty acids.

¹) From a copy kindly sent to us.

²) *Journ. chem. Soc.* **101** (1912), 1433; *Bull. Imp. Inst.* **10** (1912), 298.

Cinnamon Oil, Ceylon, German Pharmacopœia V. The market for cinnamon chips, which are chiefly used for the preparation of cinnamon oil, has undergone only slight fluctuations in the course of the summer and the prices of our distillate have therefore also remained unaltered. It is notorious that the cinnamon crop in the early months of this year was larger than had been anticipated, because as a result of the high price which ruled, the natives had cut back the shrubs more freely than usual. It is therefore feared that the principal crop, which may be later this year than is ordinarily the case, will show a not inconsiderable shortage. So far, however, we are without further information on this subject.

In the first half of the year the exports of cinnamon from Ceylon according to returns supplied by Messrs. Freudenberg & Co. of Colombo were as follows:—

	1912	1911
to Germany	370 781 lbs.	184 354 lbs.
„ Spain	276 407 „	178 805 „
„ United Kingdom . .	107 820 „	97 525 „
„ Italy	63 078 „	43 568 „
„ Holland	8 500 „	9 601 „
„ America	166 780 „	203 600 „

During the same period the shipments of cinnamon chips amounted to 1 318 059 lbs., compared with 1 300 851 lbs. in the same period of 1911.

A sample of a Ceylon cinnamon oil which had been sold in London at less than the market price by a German wholesale drug-house was submitted to us from that City for our opinion. Analysis confirmed the suspicion that the oil was sophisticated. For whereas pure Ceylon cinnamon oil has a sp. gr. from 1,023 to 1,040 and is slightly laevorotatory, the sample in question was too heavy (d_{150} 1,0423) and, singularly enough, exhibited dextrorotation ($\alpha_D + 0^\circ 11'$), these abnormalities being obviously caused by an addition of cassia oil, a much cheaper article. The exceptionally high aldehyde content of the oil (77 p. c., against a normal aldehyde content of 65 to 76 p. c.) was in harmony with this adulteration.

The oil was reputed to conform to the requirements of the British Pharmacopœia. Apart from the fact that sophisticated oils are in any case excluded from medicinal use, the oil in question would fail to pass the B. P. test on account of its sp. gr. being too high.

Citronella Oil. Since our last *Report* was published, Ceylon citronella oil has further slowly increased in price. Consumers, however, kept out of the market and fell back upon their old stocks. Then, when it became evident that the increased demands were not without justification, the sudden rush of orders drove up prices in the course of a few weeks.

reached a figure of about 1/9 d. per lb. At the same time the supplies came to a complete standstill and the sellers withdrew from the market.

The principal cause of this situation was no doubt to be found in the fact that Ceylon suffered this year from an abnormally severe and long-continued monsoon which made distilling impossible and suspended the supplies from the Interior. This was naturally calculated to cause great embarrassment to the shippers if they were to fulfil their delivery-contracts, and thus laid the foundation for an upward movement. If to this fact is added the not inconsiderable decline in the total exports of the last few years, the tightening of prices cannot be said to have been totally unexpected, although these conditions scarcely justify the actual extent of the advance.

The exports of citronella oil from Ceylon show the following figures:—

712 474 lbs.	from	January 1 st ,	1912,	to	August 12 th ,	1912,
855 589	"				in the corresponding	period of 1911,
1 068 932	"	"	"	"	"	1910,
1 106 731	"	"	"	"	"	1909.

The decline is here plainly seen. The first offers for shipment in the months of October to December came to hand in the last days of August and the quotations then receded to about 1/4 d., but of course only for oil for shipment, for the scarcity of spot stocks in Europe was not affected. It is therefore probable that until the end of the year it will be necessary to pay prices equal to about the present basis.

It is to be hoped that when supplies arrive more freely towards the end of the year the prices will settle down somewhat, although the fact must not be lost sight of that in view of the small supplies in Europe and America the first arrivals will be promptly taken out of the market, and that as a result of this the producers' and exporters' ideas of prices may not be so quickly reduced to a lower level as would otherwise be the case.

The diagram between pp. 40 and 41 shows the quantities of Ceylon citronella oil exported between the years 1892 and 1911/12, as well as the prices "cif. London".

Java citronella oil has also been very scarce of late, and all arrivals found immediate buyers at rising prices. It is obvious that the boom in Ceylon oil is partly responsible for the increased cost of the Java product. The latest reports are to the effect that the Java producers are thinking of much higher prices still for next year's deliveries, but they will only be able to carry out their intention if Ceylon does not return to the low rates which prevailed at the beginning of the year.

In the last *Bericht* of Roure-Bertrand Fils, J. Dupont and L. Labaune¹⁾ recommend a method for the direct estimation of geraniol in citronella oil.

The basis of this method is that the citronellal is first converted into its oxime; the oil is then acetylated, and after this the ester-value of the acetylated oil is determined. When the oximated oil is heated with acetic anhydride the citronellal oxime is converted into the nitrile of citronellic acid which, under saponification, is stable towards the alkali. Hence only the alcoholic constituents react, but these of course do not represent only the geraniol which is present, but the total alcohols of the oil. Dupont and Labaune proceed as follows: 10 g. citronella oil are first shaken up at ordinary temperature (15 to 18°) for 2 hours with a hydroxylamine solution²⁾. The oximated oil is then again dried and subsequently acetylated. The geraniol-content is next estimated from the ester-value of the acetylated oil and the citronellal-content by subtraction from the so-called total geraniol. As the molecular weights of citronellal (154) and of the nitrile of citronellic acid (151) correspond very nearly, the conversion of citronellal may be disregarded in the calculation. The citronellal regenerated from the bisulphite compound which the authors employed in their experiments was first tested by them for purity by the method above-described; this manipulation showed that 2,5 p. c. of an alcohol $C_{10}H_{18}O$, doubtless *isopulegol*, were present. Taking this source of error into account, the authors obtained correct values for artificial mixtures of geraniol and citronellal.

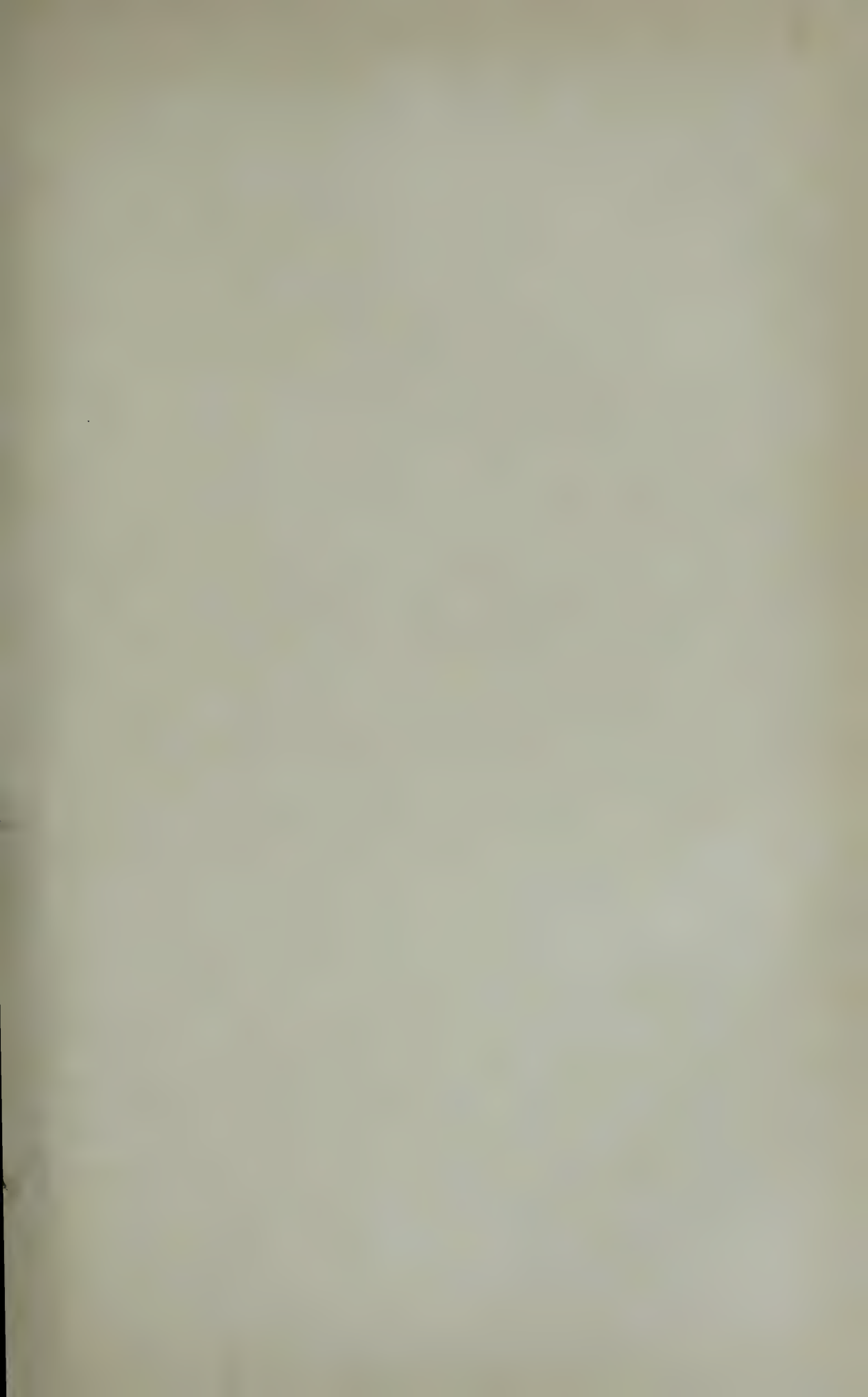
Dupont and Labaune found a Ceylon citronella oil to contain: so-called total geraniol 60,2 p. c., geraniol 43 p. c., citronellal $60,2 - 43 = 17,2$ p. c. In a Java oil³⁾ they found: so-called total geraniol 83 p. c., geraniol 43 p. c., citronellal $83 - 43 = 40$ p. c.

Such a method, provided it gives useful results, is undoubtedly of great practical value. We have therefore thoroughly investigated it, repeating in part the experiments described and partly carrying out new manipulations which appeared to us to be necessary. As the authors adopt a somewhat different acetylation method, (they heat the oil $1\frac{1}{2}$ hours with double its volume of acetic anhydride without the addition of sodium acetate), we have also carried out this method, in which we have found, that although geraniol may be acetylated quantitatively without sodium acetate, citronellal can only be very imperfectly acetylated in this way. Of an entirely pure preparation ($d_{40} 0,8562$; $\alpha_D + 10^\circ 42'$) only 25,5 p. c. was converted into *isopulegyl* acetate by this method. And although it does not matter much whether the acetylation of the oil freed from citron-

¹⁾ *Berichte von Roure-Bertrand Fils*, April 1912, 3

²⁾ Hydroxylamine solution: dissolve 10 g. hydroxylamine hydrochloride and 12 g. potassium carbonate each in 25 g. water, mix the solutions, and filter.

³⁾ In Java citronella oil, Dupont and Labaune detected two new constituents: *isoamyl*-alcohol and *isovaleraldehyde*.



Ceylon Citronella oil 1892 to 1911/12.

22

21

20

19

18

17

16

15

14

13

12

11

10

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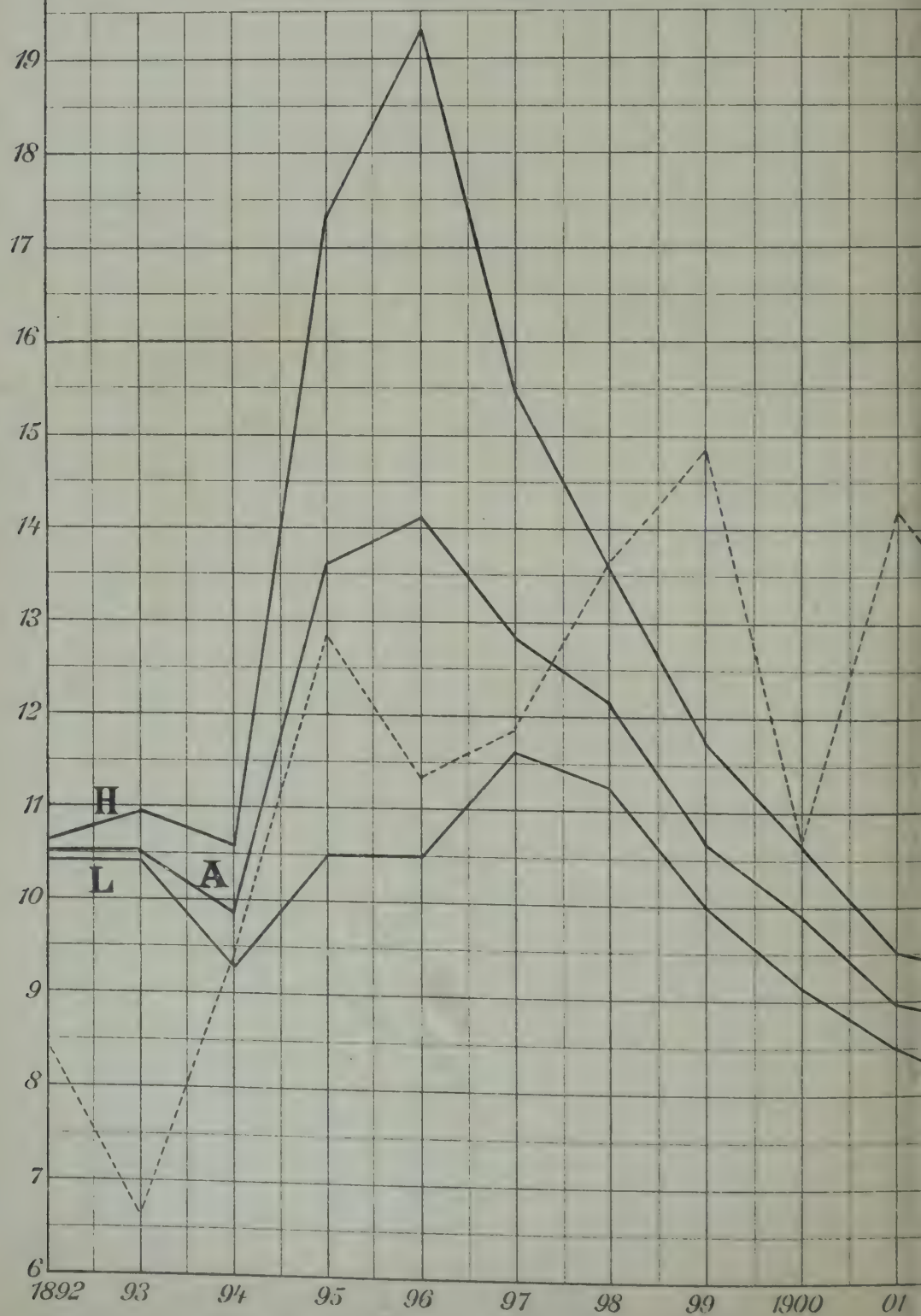
----- Quantities of oil exported, unity 100,000 lbs.

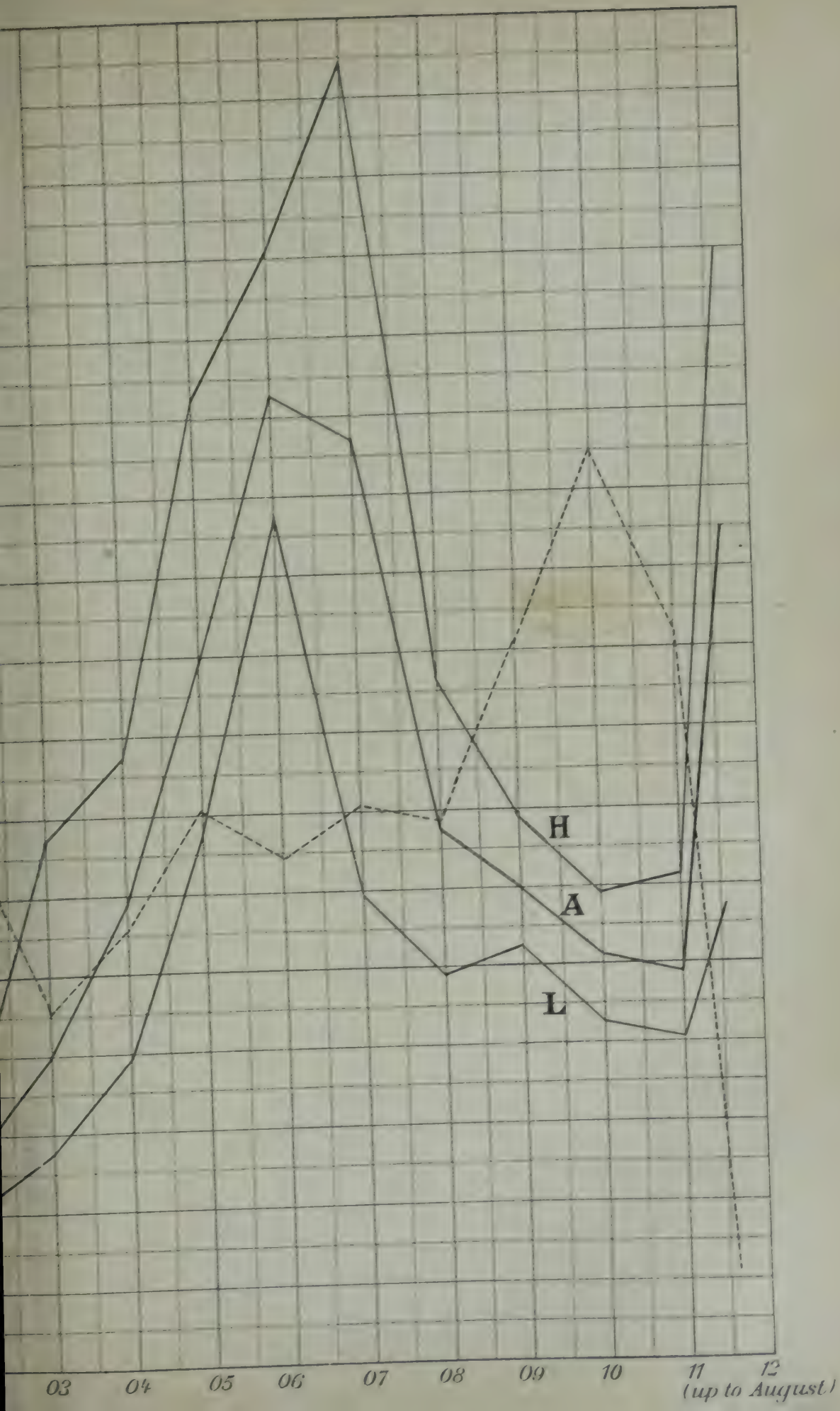
———— Prices cif London, in pence per lb., viz.,

H = highest quotation of the year.,

L = lowest id.,

A = average quotation of the different months







ellal is carried out in one way or in another, we think it necessary, in order that errors may be avoided, to point out that with the original oil the acetylation method is a matter of considerable importance. With such oil it is absolutely necessary to acetylate with the addition of sodium acetate; the best way of doing so being by the method frequently quoted by us for citronella oil. This consists in keeping each 10 g. of oil and acetic anhydride with 2 g. melted sodium acetate to boil uniformly on the sand-bath for 2 hours.

We have tried the oximation method in the first place upon several citronellal-samples of our own manufacture, and have found that after oximation and after most careful purification the proportion of acetylisable constituents in these samples was considerably in excess of 2,5 p. c. Whether this is the fault of the method or whether the sensitive citronellal is partly readily converted into another compound, cannot be said for certain. The characters of a citronellal which had been kept for some time in a closed bottle were as follow: b. p. 65 to 66° (5 mm.), d_{150} 0,8659, $\alpha_D + 9^\circ 34'$, n_{D200} 1,44962, sol. in 3,5 vols. a. m. 70 p. c. alcohol. After acetylation we found 100,6 p. c. $C_{10}H_{18}O$ and after oximation 22 p. c., showing a citronellal-content of 100,6 — 22 = 78,6 p. c. We then tried to separate the citronellal from the isopulegol (which is more soluble in water), by fractionation and by repeated steam-distillation, but we only succeeded imperfectly in doing so.

As it was impossible to obtain a pure product by this means, the aldehyde was regenerated from the carefully purified bisulphite compound and was purified by steam-distillation: d_{150} 0,8562, $\alpha_D + 10^\circ 47'$, n_{D200} 1,44561, sol. in 5 vols. a. m. 70 p. c. alcohol. The viscous and almost odourless oxime obtained from this pure citronellal gave d_{150} 0,9083; $\alpha_D - 7^\circ 40'$; n_{D200} 1,47151; sol. in 4 vols. a. m. 60 p. c. alcohol; sap. v. 1,5. After one hour's acetylation of the oxime we found 13,3 p. c. $C_{10}H_{18}O$, or consequently 86,7 p. c. citronellal; after 1½ hours heating with acetic anhydride according to Dupont and Labaune, 88,5 p. c. In order to discover whether possibly the oxime still contained aldehydic constituents it was oximated afresh. Subsequent acetylation once more gave only 87 p. c. citronellal.

We have already expressed the surmise that the differences in the estimation of citronellal may possibly be due to its instability which, as experiments showed, manifests itself in its constants after a short time.

A sample gave d_{150} 0,8598, $\alpha_D + 9^\circ 38'$. After 4 weeks the constants of the sample, which had been kept in a half-filled bottle, were d_{150} 0,8619, $\alpha_D + 9^\circ 50'$.

A sample recovered from the bisulphite compound gave at first d_{150} 0,8574, $\alpha_D + 10^\circ 31'$; after 6 weeks it gave d_{150} 0,8730, $\alpha_D + 10^\circ 50'$.

In addition to our experiments with pure citronellal we have also tried the method with mixtures of known aldehyde content. These mixtures have also been employed in the other methods mentioned below

and are here, for the sake of brevity, referred to as Ceylon oil mixture and Java oil mixture respectively.

Ceylon oil mixture: —

15 % Citronellal (80 p. c.; oximation method),
45 % Geraniol (99 % $C_{10}H_{18}O$) and
40 % Limonene (distilled over sodium)
The so-called total geraniol content was 61 p. c.

Java oil mixture: —

50 % Citronellal (80 %),
40 % Geraniol,
10 % Limonene,
So-called total geraniol content 92 %.

The following three oils were also examined: —

Ceylon oil I d_{150} 0,9065; α_D $-11^\circ 40'$; n_{D200} 1,48325;
so-called total geraniol content 61,7 %.

Ceylon oil II So-called total geraniol content 52,6 %.

Java oil . . . d_{150} 0,8848; α_D $-4^\circ 50'$; n_{D200} 1,46559;
so-called total geraniol content 83,8 %;
after 4 weeks d_{150} 0,8902; α_D $-4^\circ 40'$.

After oximation we found: —

Ceylon oil mixture	49,3%	Geraniol, therefore	61	— 49,3 =	11,7%	Citronellal
Java oil mixture	49,0%	"	92	— 49,0 =	43,0%	"
Ceylon oil I . . .	55,2%	"	61,7	— 55,2 =	6,5%	"
Ceylon oil II . . .	45,9%	"	52,6	— 45,9 =	6,7%	"
Java oil	37,2%	"	83,8	— 37,2 =	46,6%	"
" after 4 weeks	40,3%	"	83,8	— 40,3 =	43,5%	"

The results of several estimations resembled each other highly; it was immaterial whether the oximated oil had been acetylated and saponified 1 hour or 2 hours; neither did it any longer possess a citronellal odour. Assuming that the preparation used only contained about 80 p. c. citronellal, the mixtures agree well, and the method is serviceable for the determination of citronellal in citronella oil. But it does not reveal the actual geraniol-content of the oil, because other alcohols besides geraniol are present and also enter in reaction during acetylation.

In this connection we welcomed the occasion to try other testing-methods for purposes of comparison, the more readily so because from another quarter a further method was communicated to us, to which we shall refer in detail later on.

So far as our present experiments go, the estimation of citronellal in addition to geraniol by formylation (boiling the oil with twice its volume

of strong formic acid), gives insufficient results, and it will therefore probably be necessary to abandon this method. According to it, the mixtures and oils referred to above yielded the following results:—

Ceylon oil mixture	11 p.c. citronellal
Java oil mixture	15,5 " "
Ceylon oil I (so-called total geraniol 61,7)	20,2 " "
" " II (" " " 52,6)	16,9 " "
Java oil	24,1 " "
Citronellal (80 p.c.)	28,0 " "
Geraniol	11,15 " $C_{10}H_{18}O$.

The value found for geraniol explains also why, when citronellol is estimated by this method (comp. Gildemeister, *Die ätherischen Öle*, 2nd edition Vol. I, 600), the citronellol-values are somewhat too high.

On the other hand, the method recommended by us¹⁾ for the separate estimation of geraniol with phthalic anhydride proved to be very serviceable indeed; only, the assumption that the proportion of citronellal which is present in the oil can be ascertained by the simple subtraction of the geraniol-content from the content of acetylisable constituents is incorrect, for the recognised methods of estimating citronellal invariably give much lower values than those of the difference in question. In concluding we will again refer to this matter.

The method is carried out as follows:—

About 2 g. phthalic anhydride and 2 g. of the oil under examination are heated on the water-bath for 2 hours with 2 cc. benzene in an acetylation flask. The mixture is then left to cool and is shaken for 10 minutes with 60 cc. aqueous seminormal potash-solution. During this manipulation the flask is stoppered with a ground glass stopper. At the end of this time all the anhydride is converted into neutral potassium phthalate and the acid geraniol ester into its potash-salt. The excess of alkali is now titrated back with seminormal sulphuric acid. By deducting from the quantity of alkali which corresponds to the phthalic acid used in the experiment, the quantity consumed in the reaction, the equivalent in alkali of the geraniol which has been combined with the phthalic acid is obtained, and from this result the percentage of geraniol is calculated.

The experiments with phthalic anhydride gave:—

for the Ceylon oil mixture	47,9 % geraniol
" " Java " "	41,1 % "
" Ceylon oil I (so-called total geraniol 61,7 %)	34,4 % "
" " " II (" " " 52,6 %)	29,6 % "
" Java " (" " " 83,8 %)	26,6 % "
Java oil after 4 weeks	27,6 % "

¹⁾ Report October 1899, 19; April 1900, 14.

The phenylhydrazine method recommended by Kleber for the estimation of citral and citronellal (comp. *Report* April 1912, 75) gave the following values for citronellal after 1 hour's reaction:—

Ceylon oil mixture	12,4 and 13,5 %
Java " "	47,3 %
Ceylon " II	7,5 and 9,3 %
Java "	36,4 %

After about 4 weeks the experiments were repeated, the reacting of the phenylhydrazine solution being extended to $1\frac{1}{2}$ hours:—

Ceylon oil mixture	14,8 %
Java " "	41,4 %
Ceylon " I	8,4 %
" " II	10,0 %
Java "	41,3 %
" " after $\frac{3}{4}$ hours	33,2 %
" " " 1 hour	35,7 %

From the above it would appear that in mixtures of a high percentage the citronellal after 1 hour had not yet combined completely with the phenylhydrazine, but on the other hand it is also possible that a partial conversion into *isopulegol* takes place. This may be surmised *inter alia* from the fact that the 4 weeks' old Java oil mixture, in spite of having been left standing $1\frac{1}{2}$ hours, did not give higher, but on the contrary lower values with the phenylhydrazine solution than it did at first after 1 hour's standing. The experiments on this subject are being continued, regard being had to the constants of the citronellal used and to the time of action of the phenylhydrazine.

Another method for estimating geraniol and citronellal in citronella oils has been worked out lately by M. V. Boulez, who has kindly given us some particulars of it in writing. He proceeds as follows: 25 or 50 g. oil are shaken up in an Erlenmeyer flask with 100 or 200 g. of bisulphite solution saturated with neutral sulphite, and left standing for 2 to 3 hours until the aldehyde has been completely bound. 100 or 200 g. water are then added and the mixture is heated several hours in a reflux condenser with frequent stirring, until a complete separation has been effected between the oil-layer and the aldehyde compound, which latter has dissolved in the form of a sulphonic acid. The oil is now isolated in a separator, weighed and acetylated. The loss of oil corresponds with the quantity of citronellal which is present in the oil, and the geraniol-content is shown by acetylating the undissolved oil. The bisulphite solution is said to be also serviceable for the separation of other aldehydes.

For a Ceylon oil with a so-called total geraniol content of 62,07 p.c. Boulez found the following values: citronellal 18 p.c., geraniol 44,28 p.c.

= 62,28 p.c.; for a Java oil with a so-called total geraniol content of 84,50 p.c. he found 63 p.c. citronellal and 35,56 p.c. geraniol = 98,56 p.c. It is worthy of note that the sum total of citronellal and geraniol found in the Java oil considerably exceeds the total geraniol content.

When the method was submitted to a control-test it was discovered that, with an increasing citronellal-content, the solubility of the oil which does not react with bisulphite (especially of the geraniol), becomes so great as to make the values given by the method for oils of high citronellal-content much too high, the reason being that the oil which has been dissolved in the liquor is taken into the calculation as citronellal. We found, for instance, that in a mixture of 20 g. citronellal and 5 g. geraniol, after treatment with 100 g. bisulphite solution and 100 g. water and warming, the entire geraniol had dissolved clearly and that in cooling only a very small proportion of oil was separated out, and when we extracted the cooled-down solution with ether, only about 80 p.c. of the geraniol used was recoverable.

It was further shown that one hour's heating on the water-bath is quite sufficient to bring about the separation of oil and water.

Experiments by Boulez' method have afforded us the following values with 1 hour's heating:—

the Ceylon oil mixture	17	p. c.	citronellal	and	42,5	p. c.	geraniol	=	59,5	p. c.
" Java oil mixture	55	"	"	"	41,9	"	"	=	96,9	"
Ceylon oil I	7	"	"	"	51,0	"	"	=	58,0	"
" " II	6	"	"	"	44,5	"	"	=	50,5	"
Java oil	54	"	"	"	24,8	"	"	=	78,8	"

With the Java oil mixture a citronellal-content of 60 p.c. and more was repeatedly ascertained. As the unchanged oil can only be very imperfectly recovered from the liquor, even with ether, this method, as already stated, is unsuitable for oils with a high citronellal-content, that is to say for Java citronella oils, but on the other hand it may be found very serviceable for the examination of Ceylon citronella oil.

From what has been said above the conclusion may be drawn that the separate determination of both geraniol and citronellal in citronella oil is possible. For the former the phthalic anhydride method is the only one which is of any value, as in all the other methods, in addition to geraniol, the other alcohols which are present in the oil are also estimated at the same time. For determining the citronellal-content the oximation-method is suitable, and it is probable that the phenylhydrazine method recommended by Kleber may also be applicable for this purpose, but with regard to the latter further experiments are necessary. In the case of Ceylon citronella oils the citronellal-content may be ascertained by the method of Boulez.

It must however be borne in mind that with every method, when used by itself, it is only possible to estimate one of the two constituents and not, as has been the practice hitherto, to estimate both constituents by means of subtraction from the so-called total-geraniol. The reason of this is that in the case of citronella oils, in addition to geraniol and citronellal, esters and alcoholic constituents also occur, and that there is consequently a considerable difference between the so-called total geraniol and the sum of geraniol plus citronellal. For this reason we intend in future, when dealing with Ceylon as well as with Java-citronella oil, to refer no longer simply to "total geraniol", but to "so-called total geraniol", as has been done in the present article.

A fairly accurate idea of the correct constitution of the oil may be obtained by determining, in addition to the so-called total geraniol-content, the geraniol-content by the phthalic anhydride method and the citronellal-content by oximation. By applying this method we found the following values: For the Ceylon oil I: 61,7 p. c. so-called total geraniol, 6,5 p. c. citronellal, 34,4 p. c. free geraniol; for the Java oil: 83,8 p. c. so-called total geraniol, 26,6 p. c. free geraniol, 46,6 p. c. citronellal; after 4 weeks 43,4 p. c. citronellal.

We have also saponified the oils and the mixtures, when the Ceylon oils were found to show a comparatively high ester ester content, which, however, is partly only apparent, because citronellal also uses up potash. But in any case the results possess a comparative value, provided the manipulation be always carried out under similar conditions.

Ceylon oil mixture	Acid v. = 0,6	Ester v. = 1,5	
Java oil mixture . . .	" " = 0,9	" " = 2,8	
Ceylon oil I . . .	" " = 0,9	" " = 44,8	= 15,7 % geranyl acetate
Ceylon oil II . . .	" " = 1,5	" " = 33,6	
Java oil	" " = 1,5	" " = 13,0.	

The above probably explains in part the difference between so-called total geraniol and the sum of geraniol plus citronellal.

In the table (page 47) given below are set forth the results obtained by the various methods of estimation. This review may contribute to make plainer the particulars given in the foregoing pages, while it also affords the best means of forming an opinion of the value of each separate method.

Durrans¹⁾ has attempted to decide by experiment whether in the acetylation of citronella oil the added sodium acetate plays the part of a catalysing or of a dehydrating agent²⁾. He admits having failed to arrive at a conclusive result, but he believes that from his experiments

¹⁾ *Perfum. and Essent. Oil Record* 8 (1912), 123.

²⁾ *Comp. Report* October 1911, 35; April 1912, 51.

	So-called total geraniol (est. by acetylation)		Oximation	Formylation	Phthalic method	Kleber's Method		Boulez' method
						Time of reaction 1½ hour	Time of reaction 1 hour	
ylon oil mixture								
0% Citronellal	61 9/10	{ Citronellal	11,7 0/10	11,0 0/10	13,1 0/10	14,8 0/10	12,4 0/10; 13,5 0/10	17,0 0/10
0% Geraniol			49,8 0/10	50,0 0/10	47,9 0/10	46,2 0/10	48,6 0/10; 47,5 0/10	42,5 0/10
0% Limonene								
a oil mixture								
0% Citronellal	92 9/10	{ Citronellal	43,0 0/10	15,5 0/10	50,9 0/10	41,4 0/10	47,8 0/10	55,0 0/10; 60,0 0/10
0% Geraniol			49,0 0/10	76,5 0/10	41,1 0/10	50,6 0/10	44,7 0/10	41,9 0/10
0% Limonene								
Ceylon Citronella oil I	61,7 9/10	{ Citronellal	6,5 0/10	20,2 0/10	27,3 0/10	8,4 0/10	—	7,0 0/10
			55,2 0/10	41,5 0/10	34,4 0/10	53,3 0/10	—	51,0 0/10
Ceylon Citronella oil II	52,6 9/10	{ Citronellal	6,7 0/10	16,9 0/10	23,0 0/10	10,0 0/10	7,5 0/10; 9,8 0/10	6,0 0/10
			45,9 0/10	35,7 0/10	29,6 0/10	42,6 0/10	45,1 0/10; 43,3 0/10	44,5 0/10
Java Citronella oil	83,8 9/10	{ Citronellal	46,6 0/10; 43,5 0/10	24,1 0/10	57,2 0/10	41,3 0/10	36,4 0/10	54,0 0/10
			37,2 0/10; 40,3 0/10	59,7 0/10	26,6 0/10	42,5 0/10	47,4 0/10	24,8 0/10

The figures printed in black type are the values ascertained according to the separate methods, while the other figures have been obtained by subtracting these values from the so-called total geraniol.

He is warranted in concluding that, in the manipulation in question, sodium acetate probably acts as a dehydrating agent. In his opinion the fact that all quantities of sodium acetate do not affect the process of reaction in the same degree (as is the case with other catalysers), speaks against the theory of a purely catalytic action of the salt.

It is not quite clear why Durrans should again discuss the dehydrating action of sodium acetate, for seeing that (as every book on chemistry shows) no water whatsoever is formed in the process of acetylation, the question, so far as this aspect is concerned, is settled in advance.

On p. 42 of our *Report* of October 1909 we mentioned the surmise expressed by Jowitt that Lenabatu grass is the product of the hybridisation of Winter's grass (*Maha Pengiri*) with Mana grass. More recent research supports the theory that Lenabatu grass is a bastard plant¹). Accordingly, at the Imperial Institute, the parent-plants, Mana grass and Maha-Pengiri grass, were found to yield 0,20 and 0,62 p. c. oil respectively, whereas the hybrid, Lenabatu grass, yielded 0,49 p. c.

Clove Oil. As usual, in trying to form an opinion of the clove-market, there are only rumours or surmises to guide one. The reports of the present year's summer-crop, which were very favourable indeed at first, finally proved to have been too optimistic and at the moment the yield is estimated not to exceed 60 000 bales. Compared with the record-

¹) *Bull. Imp. Inst.* 10 (1912), 299.

crop of the winter from 1911/12, which is said to have amounted to about 200 000 bales, the present estimate certainly appears to be moderate, and as a result the prices began to tighten in July, while apart from a passing dullness which has manifested itself during the past few weeks, a firm tendency has ruled throughout. As there are no heavy stocks in the principal clove-centres, and as moreover a strong demand is expected from Bombay on account of the favourable outlook for the Indian harvest, an important turnover in cloves at rising prices is prophesied for the next few months. We are of course unable to assume any responsibility for these reports, and must leave it entirely to our friends' judgment whether or not they will now cover their requirements. In any case we have considerable supplies at our disposal and for the present we are still able to offer at advantageous prices even for distant delivery. Clove stems have remained dear, and were it not that our industry still holds important stocks, the prices of clove stem oil would have risen already. On the present occasion no statistical data relating to the clove market are available.

A form of adulteration of clove oil never before observed has lately been discovered in our laboratory. The sample in question, which had been submitted to our opinion from England, showed the following constants: d_{150} 1,0509, $\alpha_D + 0^\circ 30'$, eugenol content 82 p. c., sol. in 1,5 vols. 70 p. c. alcohol; with more than 3 vols. cloudiness. It was possible that the imperfect solubility might be connected with the origin of the oil, inasmuch as similar behaviour in this respect has been observed by us in oils from Amboyna and Seychelles cloves¹⁾. But the fact that the sample was dextrorotatory, which is quite abnormal in clove oil, was very suspicious. Another peculiar feature was the optical behaviour of the non-phenols, which had remained behind after the oil had been treated with 3 p. c. soda liquor. It was to be expected that these residual non-phenols would be considerably more dextrorotatory than the original oil: as a matter of fact, singularly enough, they were lævorotatory ($\alpha_D - 1^\circ 15'$). These contradictions, however, were soon explained. When the oil was treated with steam a residue of 10 p. c. was left behind, which from its properties (sap. v. 179, sol. in 90 p. c. alcohol, insol. in light petroleum), betrayed itself as castor oil. Castor oil being dextrorotatory, the reason of the dextrorotation of the clove oil sample was disclosed, as was also the reason why, this notwithstanding, the non-phenols were lævorotatory. For when the clove oil was treated with soda liquor part of the castor oil had been removed by saponification along with the eugenol, and, that being so, the normal lævorotation of the non-phenols again found expression. Needless to say, this clove oil had been sold very cheaply!

¹⁾ Report April 1912, 57.

Oil of Clove Stems. From the highest boiling fractions of oil of clove stems (b. p. 143 to 155° at 9 mm.; $\alpha_D - 21^\circ$; $d_{200} 0,966$; $n_{D200} 1,5010$) F. W. Semmler and E. W. Mayer¹⁾ have isolated a sesquiterpene alcohol $C_{15}H_{26}O$, which they found to possess the following constants: b. p. 138 to 148° (8 mm.), $d_{200} 0,9681$, $\alpha_D - 17^\circ$, $n_D 1,5010$, mol. refr. found 68,18, calc. for $C_{15}H_{26}O$ 68,07. Judging from these values the body is a bicyclic sesquiterpene alcohol with one double bond. The chloride of the alcohol (b. p. 147 to 155° at 12 mm.; $d_{200} 0,990$) when treated with alcoholic potash liquor yields a hydrocarbon possessing the following properties: b. p. 123 to 126° (10 mm.), $d_{200} 0,9273$, $\alpha_{D200} - 23^\circ$, $n_{D200} 1,5024$.

Oil of Convolvulus Scammonia. F. B. Power and H. Rogerson²⁾ have obtained from the root of *Convolvulus Scammonia*, L. (N. O. Convolvulaceæ), by steam-distillation of the alcoholic extract, a trace of a reddish-yellow oil with a powerful odour, in which the presence of furfurol was determined by the colour-reaction.

Copaiba Balsam Oil. According to E. Deussen and B. Eger³⁾, the preparation of β -nitrocaryophyllene⁴⁾ from copaiba balsam oil is of great importance in the estimation of the last-named product. So far as the material of investigation at present available goes, the limits of value for the yield of nitro-product are from 14 to 16 p. c. for Pará- and from 5 to 8 p. c. for Maracaibo oil.

The authors present the results of their investigations with copaiba balsam oils of different origin, as well as with mixtures of copaiba balsam oils with African copaiba balsam oil and with gurjun balsam oil in the form of a table.

The exact proof of the presence of gurjun balsam oil in copaiba balsam oil is only afforded by the preparation of the gurjunene ketone semicarbazone⁵⁾. For this purpose 170 g. oil is split up at 10 to 12 mm. press. up to a temperature of about 145° C., into three fractions of 50 g. each, the fraction which boils above 145° C. being disregarded. Each of the three fractions is oxidised with potassium permanganate in acetone solution. Apart from its m. p. (234° from boiling alcohol) the high sp. rotation ($+ 317^\circ$ in concentrated aqueous chloral hydrate solution) is characteristic of the semicarbazone. Another indication of the presence of gurjun balsam oil is afforded by Turner's reaction. Deussen and Eger dissolved 1 drop of the material under examination in 3 cc. glacial acetic acid, added 2 drops of a freshly-prepared 1 p. c. sodium nitrite solution and layered the solution carefully over concentrated sulphuric acid. When the

¹⁾ Berl. Berichte 45 (1912) 1392.

²⁾ Journ. chem. Soc. 101 (1912), 398.

³⁾ Chem. Ztg. 36 (1912), 561.

⁴⁾ See p. 148.

⁵⁾ Comp. Report April 1910, 146; April 1912, 109

glacial acetic acid solution acquires a deep violet colour within 5 minutes the presence of gurjun balsam oil is to be assumed.

Coriander Oil. It is true that in the course of the summer a few considerable parcels of Russian oil made their appearance, but these in no way affected the position of the market and the price remained unaltered. The reports which have recently been received from Russia, and which speak of a poor crop, have also failed to make any impression and the article continues to suffer from the neglect to which reference has already been made in the past. It would appear that considerable supplies still exist in second hands. Unfortunately Russia is the only producing centre which counts.

Cubeb Oil. Suitable parcels of cubebs have been offering very sparingly and when they made their appearance high prices had to be paid for them. Hence our quotations for cubeb oil have remained unchanged and high during the summer. The high prices, however, have had no effect at all on the demand.

We learn from an article by J. C. Umney and H. V. Potter¹⁾ that a parcel of cubebs imported from Macassar into Amsterdam, and distilled there, yielded an oil which attracted attention by its extraordinarily low optical rotation. Whereas this value ranges normally from -25 to -40° ²⁾ in the oil in question it was only -14° . The cubebs themselves appeared to be in most respects normal, but the odour was mace-like.

The abnormality of this oil led the authors to make some enquiries as to the cubebs present on the London and Amsterdam drug markets, with the unsatisfactory result that out of eight samples examined, only four proved to be genuine cubebs. Three samples consisted of other species of cubebs, while one contained an admixture of other fruits. Part of the samples was also largely adulterated with stalks, in one instance to the extent of 46 p. c. The spurious cubebs differed from the genuine both by their mace-like odour and by the result of the sulphuric acid test. For when the fruit, crushed in a porcelain basin, was moistened with a little concentrated sulphuric acid, the genuine samples quickly showed a beautiful crimson colour, while in the case of the false fruits the colour was yellowish brown. It is stated that the difference is still more easily perceptible in the ethereal extract of the fruit, of which extract, moreover, the genuine cubebs yield more (20 to 25 p. c.) than does the spurious fruit (only about 15 p. c.). There was also a difference in the microscopical characters of the various species.

¹⁾ *Chemist and Druggist* 80 (1912), 331, 443.

²⁾ Umney and Potter give -30° as the maximum limit of value. This is probably a misprint.

The authors suspect that the spurious cubebs consist partly of the fruit of *Piper ribesoides*, Wall. and partly of an as yet unknown variety of *Piper*. The latter, when subjected to steam distillation¹⁾, yielded 4 p. c. of essential oil of a decided mace odour: $d_{20} 0.894$, $n_D^{20} + 16^\circ$, sap. v. 0, ester v. after acetyl. 56.1. Genuine cubebs, distilled for purposes of comparison, yielded more than twice that percentage of oil. with sp. g. 0.917, and opt. rot. — 43° .

The behaviour under fractionation of the two distillates also showed marked differences. The oil from the spurious cubebs began to boil below 160° ; one-half of it passed over up to 200° , and a further 30 p. c. between 200 and 270° . On the other hand, of the oil from the genuine cubebs, only 5 p. c. passed over below 200° , 85 p. c. passing over between 200 and 270° .

The surmise that the false fruits might be identical with those of *Piper Lowong*, Bl., which were distilled by Peinemann²⁾ several years ago, proved to be unfounded, the microscopical structure of the two *piper*-species being entirely different. Umney and Potter conclude that certain of the abnormal oils of commerce are produced from mixtures of the genuine berries either with this hitherto unidentified, or with other varieties. This would also explain the abnormality of the Amsterdam oil referred to at the beginning of this paragraph.

J. Small³⁾, and E. M. Holmes⁴⁾ also give their views on the same subject. Small has examined several authentic samples of genuine and spurious cubebs, placed at his disposal by the Herbarium and the Museum in London of the Pharmaceutical Society, and, basing himself upon his observations on these, has examined a number of commercial samples. Among genuine cubebs, Small examined several varieties of *Piper Cubeba*, among them *P. C.* var. *Rinoe Katoentjar* and *P. C.* var. *Rinoe tjaloeroek*; among the spurious fruits were *P. C.* var. *Rinoe badak*, *Piper ribesoides*, Wall. and *Piper crassipes*, Korth. Out of five commercial samples, four proved to be heavily adulterated with fruits of *Rinoe badak*. Holmes calls particular attention to the poisonous character of *Rinoe badak*, which is a native of Java and is there regarded as a genuine cubeb. It is easily detected by its mace-like odour and by the sulphuric acid test mentioned above.

In addition to those already mentioned by Small, Holmes cites the following plants as producing spurious cubebs: *Piper Lowong*, Blume, *P. venosum*, C. D. C. and *P. mollissimum*, Blume, also *Tethranthera citrata*, *Bridelia tomentosa*, and *Rhamnus*-species. The fruits of *Piper mollissimum* are known in Java as *Keboe*-Cubebs. The berries of *P. ribesoides* have a

¹⁾ *Perfum. and Essent. Oil Record* 3 (1912), 64.

²⁾ *Arch. der Pharm.* 234 (1896), 238.

³⁾ *Pharmaceutical Journ.* 88 (1912), 639.

⁴⁾ *Perfum. and Essent. Oil Record* 3 (1912), 125.

somewhat acrid, and those of *P. crassipes* a cajeput-like odour. *Rinoe badal* is said to be the only poisonous species.

The articles by Holmes and Small are of purely pharmacognostical interest, and for particulars of their contents we must therefore refer to the originals.

Cumin Oil. There has been no scarcity of distilling material, and in any rate there has not been the slightest difficulty in supplying the small demand for cumin oil, the employment of which appears to be declining fast.

Oil of *Cymbopogon coloratus*. In our April *Report* of 1911 (p. 58) we referred to an oil prepared in the Fiji Islands from *Cymbopogon coloratus* Stapf, which is known there by the name of lemongrass oil, but which in its characters, stands between lemongrass and citronella oil. The Imperial Institute in London¹⁾ now describes, together with this same oil, three further distillates of the same species of grass. The odour of all the four samples was similar, reminding at the same time of citronella and of lemongrass oil; the colour varied from golden yellow to brown; a rectified oil was of somewhat paler colour. Further examination of the crude oils gave the following results: d_{150} 0,9155 to 0,920, α_D $-7^\circ 43'$ to $-8^\circ 40'$, geraniol 15,6 p. c., citronellal 45,7 to 49,5 p. c.; constituents reacting with bisulphite from 42,0 to 43,5 p. c. The oils gave clear solutions with 1 and more vols. 80 p. c. alcohol; in 70 p. c. alcohol they were either insoluble, or the solution (which was clear in the proportion of 1:3) turned cloudy when more alcohol was added. The rectified oil showed a similar degree of solubility, and its other characters were as follow: d_{150} 0,9111, α_D $-10^\circ 42'$; constituents reacting with bisulphite 42 p. c. The Imperial Institute had procured from Fiji samples of the grass, all of which were identified in the London botanic gardens as *Cymbopogon coloratus*, Stapf, a species of grass of which the essential oil was hitherto unknown (*Report* April 1907, 33). Enquiries by the Imperial Institute showed that the views as to the value of the oil differed; on the one hand it was thought that it would only be saleable at the price of Java citronella oil; but others are of opinion that it would find a market at a slightly lower price than lemongrass oil.

Oil of *Cymbopogon sennaarensis*. In our *Report* of April 1911, p. 58, we referred to an oil which had been forwarded to the Imperial Institute in London from the Sudan, and which was said to be derived from *Cymbopogon Iwarancusa*. Closer investigation of the grass has shown that its parent plant is *Cymbopogon sennaarensis*, Chiov.²⁾ The herb, which has an odour of pennyroyal, yielded upon distillation 1,005 p. c. oil, possessing the following properties: d_{150} 0,9383, α_{D20} $+34^\circ 14'$, total

¹⁾ *Bull. Imp. Inst.* 10 (1912), 27.

²⁾ *Bull. Imp. Inst.* 10 (1912), 31.

alcohol 17,3 p. c. From 26 to 27 p. c. reacted with sodium bisulphite. The principal constituent of the oil is an aromatic ketone resembling pulegone in its odour and its other properties; it contains further a strongly dextrorotatory terpene and other high boiling compounds.

Cypress Oil. While enlarging our factory at Barrême, in the Department of the Basses-Alpes (a matter to which reference is also made elsewhere), we made arrangements which enable us to distil cypress oil in considerably larger quantities than we have been able to do in the past. We are therefore now in a position at any time to supply whatever demand may arise for this well-established whooping-cough remedy, the popularity of which has considerably increased in recent years. The price of our quality has remained at its old level, although there has been no lack of cheap offers, which, however, mostly applied to oils with properties calculated to prejudice very greatly the excellent reputation of the article as a whooping-cough remedy. We can only repeat our warning against the use of such cheap oils.

In an article on the cypress species which occur in France in a semi-wild state, E. G. and A. Camus¹⁾ describe the two kinds which are chiefly cultivated in Southern France, namely: *Cupressus sempervirens*, L. (*C. fastigiata*, D. C.) and *C. lusitanica*, Mill. (*C. glauca*, Lamk.; *C. pendula*, l'Hérit.; *C. Uhdiana*, Gord.; *C. sinensis*, Hort.). *Cupressus sempervirens* is a native of the East, and is cultivated in the Mediterranean countries, as well as in Southern Europe, Greece, the Mediterranean Islands, Asia Minor, and Chile. With regard to the original habitat of *Cupressus lusitanica* nothing definite is known. It is grown in gardens in Portugal, Spain, and Italy and is said to have been brought to France in the year 1683. Particulars relating to the oils of the cypress are given on p. 25 of the same publication. *Cupressus lusitanica* would appear to contain the greater percentage of oil, 400 kilos branches of this species having yielded 1 kilo (= 0,25 p. c.) of oil; while 491 kilos branches of *C. sempervirens* was needed to produce the same quantity of oil.

The characters of the two oils are shown below:—

	<i>C. sempervirens</i>	<i>C. lusitanica</i>
d_{150}	0,8744	0,8723
α_D	+ 12° 6'	+ 9° 10'
Solubility in 90 p. c. alcohol	3,5 vols. & m.	3 vols. & m.
Acid v.	0,7	1,05
Sap. v.	4,9	9,8
Sap. v. after acet.	14,7	26,6.

An attempt to distil oil from the seed of *Cupressus sempervirens* was unsuccessful. On the other hand the cones, freed from seed, yielded

¹⁾ *Berichte von Roure-Bertrand Fils*, April 1912, 8.

0,415 p. c. essential oil of a bright amber colour, showing the following constants: d_{150} 0,8739, $\alpha_D + 29^\circ 52'$, acid v. 1,0, sap. v. 9,8, ester v. after acet. 21,0, sol. in 4 vols. a. m. 90 p. c. alcohol.

Delft grass oil. In our *Report* of April 1911 (p. 59), we gave some particulars of the properties of delft grass oils which had been distilled by Jowitt at Bandarawela (Ceylon) and investigated more closely by Samuel S. Pickles. The analytical figures have now also been published in the *Bulletin of the Imperial Institute* [10 (1912), 30] in London.

Dill Oil. A sufficient quantity is available of dill oil of the excellent quality which we distil exclusively from European seed. Dill seed is quoted this year at considerably higher prices than in 1911, and an advance in the oil quotations is therefore probably only a question of time.

Dutch Myrtle Oil. From the catkins of the Dutch Myrtle (*Myrica Gale*, L., N. O. Myricaceæ), C. J. Enklaar¹⁾ has distilled 0,4 to 0,6 p. c. essential oil (d_{150} 0,899; $\alpha_D - 5^\circ 36'$). The lowest boiling fractions (b. p. 162 to 163° at 760 mm.; d_{150} 0,862; $\alpha_D - 25^\circ 34'$) contained pinene; but whether α - or β -pinene, Enklaar was unable to distinguish. No nitrosochloride was obtained; oxidation with potassium permanganate yielded an acid m. p. 102 to 103°, perhaps *i*-pinonic acid or contaminated *l*-nopinic acid. It would appear that the oil contains *d*- α -phellandrene (m. p. of the nitrite 112 to 113°). The presence of cineol was proved by Enklaar by the preparation of the hydrobromide and the iodol-compound (m. p. 114°). The highest-boiling fractions of Dutch Myrtle oil contain a sesquiterpene (b. p. 150 to 152° [17 mm.]; 263 to 265° [760 mm.]; d_{150} 0,928; $\alpha_D - 4^\circ 30'$) perhaps caryophyllene. Finally, the high-boiling portions contain a sparingly soluble solid body which crystallises from alcohol in beautiful long needles and possesses an agreeable odour of Dutch myrtle.

The results of this examination show that the constitution of the oil prepared from the catkins differs from that prepared from the leaves, which latter was investigated last year by Pickles²⁾.

Essential Oils, Sicilian and Calabrian.

Our esteemed friend, Mr. Eduardo Jacob, of Messina, in his customary obliging manner reports as follows:—

In my spring-report I expressed the expectation that all the Sicilian essential oils would experience an increase in value in the course of the summer. With the exception of the case of bergamot oil, this expectation

¹⁾ *Chem. Weekblad* 9 (1912), No. 11. From a copy kindly sent to us.

²⁾ *Journ. chem. Soc.* 99 (1911), 1764. *Report* April 1912, 60.

has been realized fully and even beyond anticipation, for as a matter of fact it became clearer and clearer, as the summer went on, that the quantities of oil of the various fruits of the *agrumi* which had been produced during this year's season had fallen not inconsiderably below those produced in previous years.

Owing to the high prices which were reached in the course of the summer the consumption decreased, and it is merely because of this that the want of oil has not been more severely felt, and in the case of lemon and orange oils such a want actually does exist.

Bergamot Oil. The abnormally high prices of bergamot oil have diminished the consumption of this article to an extent which had not been anticipated, the consumers having sought and found substitutes in other and cheaper odoriferous substances. It may be boldly asserted that the consumption of bergamot oil has diminished by more than one half, and only the exceptionally small crop of last season has made it possible for the article to maintain a high level of prices in spite of the greatly reduced purchases from abroad.

The prices of bergamot oil, which stood at about 60 *M* per kilo in April of this year, have only experienced slight fluctuations during the subsequent six months, sagging at times to as low a figure as 54.55 *M* and then again advancing a few marks, an up-and-down movement which was repeated several times in the course of the summer.

In view of the smallness of the available supplies, however, even the slight demand from abroad, which was at no time entirely absent, was sufficient to maintain the oil at its high price-level.

The new flowering of the bergamot-trees did not present a particular favourable appearance from the beginning; the last winter-season had brought very little rain, the storms of January completely stripped the trees of their foliage, and the trees had not vigour enough both to put forth fresh foliage and to cause the fruit to set satisfactorily.

While therefore on the one hand the available supplies of oil are scarcely worth mentioning, it must also be borne in mind that the coming crop will fall below the average.

A favourable or unfavourable course of atmospheric conditions during the time of gathering and manufacturing, and the greater or less oil-content of the new fruit will affect the range of values of the new oil adversely or otherwise; but this much is certain, that during the coming season very high prices are still likely to rule, and that no return to the values which used to prevail before the great rise of last year set in is to be expected this season.

Assuming that no unfavourable influences obtain ascendancy during the harvesting-season, it would seem to be reasonable to expect that the price of the new bergamot oil will be about 50 *M* per kilo.

Lemon Oil. In my spring-report I expressed the view, adducing detailed grounds for the statement, that the statistical position of lemon oil was very unfavourable, and pointed to high prices. The course of events has not only shown that I was not mistaken, but has considerably and in an unforeseen manner outrun my anticipations.

At the beginning of March, when oil of lemon stood at about 15 *M* per kilo, the great coal-strike commenced in Great Britain, and not only completely suspended the whole system of intercommunications in that country, but, owing to the enormous rise in the coal-prices, made its effects felt to the furthest ends of the earth. The suspension of all industry and traffic in one of the greatest industrial countries of the world naturally brought about a declining tendency in many articles, and it did so specially in the prices of lemon oil. At any rate, the fact that the quotations of this oil during April and May gave way to no greater extent than about 15 p.c. was a proof of the intrinsically healthy position of the article. This fact is the more worthy of note because the downward tendency of the prices was supported at the same time by the local speculators in Sicily.

For it so happened that the flat period of business during the British coal-strike synchronised with the principal flowering season of the lemon trees in Sicily. The profusion of flowers held out hopes of a good harvest in the forthcoming season, and the conjunction of dulness in business and good crop-prospects induced numerous manufacturers and speculators to sell some portion of their stocks. Naturally it was only possible to do so at falling rates, and the downward grade of prices was further accentuated by the passive attitude of the foreign consumers. In this way the value of lemon oil gradually receded to 12.50 *M*, but in the first days of June it again advanced to 13.50 *M*.

This revival in the article was fostered by the circumstance that throughout the spring and the early summer the climatic conditions prevailing in Sicily were injurious to the setting, and afterwards to the development, of the fruit. The small fruit dropped in a wholesale manner and the two subsequent flowering periods of the lemon tree, towards the end of May and June respectively, also took an unfavourable course. The fears for the result of the new crop put fresh life into the article, and both foreign buyers as well as local speculators again commenced to turn their attention to the market, and afterwards to gain confidence in it.

Old lemon oil for prompt delivery rushed upwards in the course of the month of June from 13.50 *M* to 16.— *M*; in the first days of the month of August it reached the figure of 17.— *M*, and at the present time it is no longer procurable for less than 17.75 *M*. Oil of the new crop for delivery, January-March shipment, was offered during the month of April at the parity of 11.50 *M*, and during the brief slump in the month of May had fallen to 10.50 *M*. As the prospects of the new crop grew

worse it began to advance, slowly at first, and then more and more rapidly, until at the end of June it had reached a level of 13.50 *M*, at the end of July of 14.25 *M* and at the beginning of September of 15.75 *M* to 16.— *M*.

If we now ask ourselves to what extent such a pessimistic view of the position and such a relatively high price for new crop oil for delivery are justified, it is evident that no definite off-hand answer can be given. Only about one-third of the annual crop of lemons in Sicily is used for the manufacture of lemon oil; the remaining two-thirds are exported green, either boxed or in car-loads.

The larger the quantity of green lemons which is taken up by foreign and native consumers, the smaller is that which is turned into lemon oil. On the other hand, the smaller the proportion of green fruit sent abroad, the larger grows the quantity of fruit devoted to the manufacture of oil of lemon. The incalculable factor which arises from this divided use to which the lemons are put will always make it impossible to forecast with any certainty, before the commencement of the new harvest, how the course of prices of lemon oil will shape itself. But no commodity can escape the consequences of its statistical position, and within recent years the statistical position of oil of lemon has steadily grown worse and worse, and this year it is again less favourable than in 1911.

Taking the most optimistic view, and assuming that in the coming winter of 1912/13 we have to deal with a crop which does not exceed that of the seasons 1910/11 and 1911/12, the fact remains that we entered upon the manufacturing period of 1910/11 with a stock of about 100 000 kilos of old oil; that in December 1911 about 30 000 kilos of old stock were carried forward into the new season 1911/12, and that beyond any doubt the stocks which are still in existence to-day, and which can at most amount to 25 000 kilos, will have been entirely taken up by the consumers by December 1912. Hence it follows that we will enter upon the new crop without any supplies of old oil whatsoever, either at home or abroad, which can serve to tide over the requirements of the consumers for some little time at the commencement of the new year. Therefore any large accumulation of unsold supplies of lemon oil upon the Messina market during the first four or five months of the coming year appears to be out of the question.

From what has been said above the conclusion may readily be drawn that a decline of prices of the new lemon oil appears to be highly improbable, and in the most favourable case could not occur until an abundant lemon crop in 1913/14 had become an assured event. Until such a contingency occurs, this market, partly owing to the requirements of foreign countries, and partly through the manœuvres of the local speculators who will exploit this favourable opportunity, will in all probability be subject to a series of fluctuations with an upward tendency, but hardly to any important downward movements.

Mandarin Oil. As already mentioned in my last report, mandarin oil has only been produced in small quantities this year. As the existing stocks were gradually used up, the article began slowly to improve in price, and this firmness is the more likely to endure because the prospects of the new crop, so far as they can be estimated at present, are not at all promising.

Orange Oil, bitter, has moved between 17 *M* and 19 *M* throughout the summer, with only slight fluctuations, but recently with an upward tendency.

The present quotation of this oil, of which also the available supplies are but small, is 19 *M* per kilo cif. Trieste.

Orange Oil, sweet. In the month of April this oil changed hands at 17.50 *M*. During May this value was maintained, but the excellent development of the flowers, particularly in Calabria, caused the price of orange oil on the spot to fall to 16.50 *M*, while simultaneously speculative sales were made here of new oil for delivery at 15.50 *M* to 16 *M*. But the subsequent period of development of the young fruit soon destroyed the high hopes which had been entertained of the new crop. The small fruit dropped in enormous quantities, and in Sicily in particular the fruit on the trees was seriously damaged. Under these influences, and also because spot oil was getting scarcer and scarcer, the prices of old oil again rose in the second half of June to 17.50 *M* and in the first days of July they even surpassed this figure; then they stood still for a time at 18.50 *M*, and finally, quite recently, they advanced to 19 *M*.

The available supplies have gradually been cleared; at the present moment only a few very small remnants are left over and these are growing less every day. The damage suffered by the young fruit in the commencement of the summer has naturally had its effect upon the quotation of the new oil for November/December delivery.

In view of the fact that the coming orange crop will not be large, it is scarcely likely that the prices of the new oil will be lower in the course of next season, even if the climatic conditions and the oil-content of the new fruit should be favourable for the manufacture of orange oil.

Bergamot Oil. In the course of the past six months a further series of adulterated bergamot oils has been submitted to investigation in our laboratory; the principal form of sophistication being found to consist in the addition of artificial esters. In the table below we present a synopsis of several samples of this description, in which the deviations, compared with normal bergamot oils, are printed in heavy type in order to render them more distinct.

So far as specific gravity was concerned, only the first two samples, and in respect of optical rotation only samples 1, 3, 5 and 9 satisfied the

Bergamot oil	No.	1	a ¹⁾	2	a ¹⁾	3	4	a ¹⁾	5	a ¹⁾	6	a ¹⁾	7	8	9	Normal oil
d ₁₅	0,8821	—	—	0,8859	—	0,8773	0,8787	—	0,8864	—	0,8938	—	0,8796	0,8728	0,8790	0,881 to 0,886
α _D	+ 22° 50'	—	—	+ 25° 0'	—	+ 13° 20'	+ 38° 45'	—	+ 22° 35'	—	+ 35° 55'	—	+ 30° 30'	+ 27° 0'	+ 21° 30'	+ 8 to + 24°
Evap. residue	5,2%	—	—	5,8%	—	—	—	—	—	—	—	—	3,6%	15,8%	5%	4,5 to 6%
Sap. v. of evap. residue .	207,9	—	—	183,4	—	—	—	—	—	—	—	—	197,5	37,5	169,2	168 to 200
Sol. in 90 p.c. alcohol .	0,3 vols. & m.	—	—	0,4 vols. & m.	—	each vol.	0,5 vols. & m.	—	0,3 vols. & m.	—	0,5 vols. & m. dilute sol.	—	0,5 vols. & m.	insol.	0,2 vols. & m.	up to 1 vol. req. for sol.
Acid v.	2,1	—	—	4,0	—	3,0	1,2	—	1,5	—	2,3 opal.	—	1,5	1,1	2,2	1,0 to 3,5
Ester v. after 1 h. sap. with 10 cc. seminormal liquor	103,6	—	—	78,0	—	90,4	69,7	—	97,3	—	74,8	—	77,5	62,3	65,5	at least 34%
Ester content (calc. as linalyl acet.)	36,2%	—	—	27,3%	—	31,7%	24,4%	—	34,1%	—	26,2%	—	27,1%	21,8%	22,9%	
Ester v. after 2 h. sap. with 20 cc. seminormal liquor	107,6	95,5	76,8	83,2	—	89,8	74,1	76,4	105,4	106,4	80,7	85,4	81,4	62,4	66,8	Difference so far observed in fract. sap., up to 4
Ester v. after 1 h. sap. with 10 cc. seminormal liquor + 25 cc. alcohol	96,9	91,1	64,9	71,7	—	87,2	61,4	60,3	87,4	87,8	58,6	57,5	69,7	61,1	65,3	
Difference	10,7	4,4	11,9	11,5	—	2,6	12,7	16,1	18,0	18,6	22,1	27,9	11,7	1,3	1,5	Difference between sap. v. and acid v. II so far observed, up to 10.
Sap. v.	105,7	—	—	82,0	—	93,4	—	—	—	—	—	—	79,0	63,4	67,7	
Acid v. II	95,2	—	—	72,9	—	58,0	—	—	—	—	—	—	73,3	59,3	62,2	
Difference	10,5	—	—	9,1	—	35,4	—	—	—	—	—	—	5,9	4,1	5,5	
Terpinyl acetate content, about	not traceable	—	—	5%	—	not traceable	6%	—	10%	—	12%	—	suspect	not traceable	not traceable	
Esters of sparingly sol. acids	not traceable	—	not traceable	not traceable	—	present	not traceable	not traceable	not traceable	not traceable	not traceable	not traceable	not traceable	not traceable	not traceable	
Glycerol esters	0,55%	—	—	0,43%	—	not traceable	not traceable	not traceable	not traceable	not traceable	—	—	—	—	—	
Sap. v.	603,3	—	—	456,9	—	—	—	—	—	—	—	—	—	—	—	
Spirit	—	—	—	—	—	abt. 30%	—	—	—	—	—	—	—	—	—	

¹⁾ Oil rectified by steam.

requirements for bergamot oil. In most of the samples, too, the ester content (calculated from the ester value obtained after one hour's saponification of 1,5 to 2 g. of oil with 10 cc. seminormal liquor), was too low apart even from the added adulterants, and only in the case of sample No. 1 did it correspond to the ester-content of normal oils. In the last named the original ester content of about 34 p. c. was increased by the added glycerol ester by about 2 p. c. Sample No. 2 also contained glycerol ester. The detection was carried out according to the method described in detail in our *Report* of April 1911, 151, to which a brief reference will here be sufficient. Of the filtered alcoholic liquid which is obtained after shaking 10 cc. of oil with 20 cc. 5 p. c. alcohol, 10 cc. should only use up about 0,1 cc. of seminormal potash liquor after being neutralised for saponification. The samples referred to above, however, required 0,75 cc. and 0,6 cc. respectively. For the purpose of isolating the glycerol ester about 50 cc. of the oil were extracted three times with an equal volume of 5 p. c. alcohol, and by subsequent evaporation of the extracts thus obtained the quantity of added ester was estimated. In both cases it was found to be about 0,5 p. c. The presence of the ester was then indisputably established by the determination of the saponification value and the detection in connection therewith, of the presence of glycerol and acetic acid. In the case of both oils also the difference obtained in fractional saponification (*Report* October 1911, 116) was excessive, but in the course of a repeated fractional saponification of the steam-distilled oils (comp. *Report* April 1912, 79) it was found that only sample No. 2 contained terpinyl acetate, the excessive difference in No. 1 being due to resinification of the oil. The quantity of added terpinyl acetate, calculated from the difference of 11,5 as determined by us with mixtures of known content, was about 5 p. c. (*Report* October 1911, 117).

Sample No. 3 contained about 30 p. c. spirit and, in addition, an ester of a sparingly-volatile acid, the acid value II, as estimated according to our *Report* of October 1910, 61, being about 35,3 lower than the saponification value of the oil. The available quantity, however, was insufficient for the identification of the ester. When the alcohol had been removed by extraction with solution of common salt the oil gave $d_{15} 0,8984$, $\alpha_D + 18^\circ 6'$.

The next three samples (Nos. 4, 5 and 6), when subjected to fractional saponification showed excessive differences in their saponification values, and a repeated testing, carried out after the oils had been distilled with steam, showed similar differences, thus proving the presence of terpinyl acetate in the proportions indicated.

In the case of No. 7 also adulteration with terpinyl acetate was suspected, but the quantity of this oil sent to us for examination was insufficient to carry out a steam-distillation and in this case, therefore, the question whether terpinyl acetate was actually present remained unsettled. Apart from this, however, the oil would have to be rejected on account

of its specific gravity being too low, its optical rotation too high and its evaporation residue insufficient.

In contradistinction to this sample the evaporation residue of No. 8 (15,8 p. c.) was decidedly too high. Its liquid consistency, its insolubility in hot alcohol and its quite abnormally low saponification value (37,5) pointed to the presence of mineral oil. The insolubility of the oil in 90 p. c. alcohol is likewise traceable to the same addition.

In the oil referred to in the 9th column of the table no adulteration could be detected and it is therefore not impossible that its inferiority was due to the use in its manufacture, of inferior (waste) fruit.

Lemon Oil. Lemon oil consists principally of terpenes and sesquiterpenes, bodies which are of slight importance so far as the odour of the oil is concerned. These compounds are practically insoluble in 80 p. c. alcohol, whereas the constituents of the oil which are valuable from the odoriferous standpoint are readily soluble in the same alcohol. For this reason, G. Patané¹⁾ is of opinion that the determination of solubility affords a valuable criterion for the estimation of the value of lemon oil, and has based method of examination upon this property. He employs two different manipulations. The first consists in shaking up at exactly 20° in a test-tube of 10 cc. capacity, graduated to 0,1 cc., equal quantities of oil and of alcohol of a given strength. When the mixture has settled completely, the degree of increase of the alcohol-layer is read off. The second method consists in mixing equal quantities of oil and of alcohol of a given strength in the test-tube and in warming them until they are completely dissolved. The mixture is then allowed to cool under constant stirring with a thermometer graded to one-tenth degrees, until clouding ensues. When that moment arrives, the temperature is read off. Differences of temperature of 1st 10th degree are sufficient to cause clouding. All oils which have the same clouding-temperature show the same conditions of solubility in the first test, so that it becomes possible to draw up a comparative scale of clouding-temperature and solubility. If necessary, it is sufficient to apply the second test only, which can be executed quickly and at the same time is said to be very reliable.

The addition of 10 p. c. of terpenes increases the clouding-temperature by more than one degree, of 20 p. c. by about two degrees, and so on, but with this difference that as the terpene-percentage rises the intervals of temperature become smaller and smaller. Moreover, the relation between citral content and solubility is said to admit of further deductions concerning the condition of the oil.

Great care must be taken with the alcohol to be used for the test, because so slight a difference as one-tenth of a degree suffices to alter the clouding-temperature of the alcohol. According to Patané it would

¹⁾ *Per un più razionale apprezzamento delle essenze di limone.* Acireale 1912.

be desirable to use methyl alcohol instead of ethyl alcohol for the second test, because the oil is less soluble in the former, hence the clouding temperature is in excess of the atmospheric room-temperature and there is no need for artificial cooling, as would have to be done with ethyl alcohol of 93 to 94 p. c. strength.

The same test can be applied with advantage to oils of orange and mandarin, both of which are much less soluble than is lemon oil.

In estimating the solubility the fact must be taken into account that oils of different origin behave differently, as the condition of the soil affects the constitution of the oil.

A comparatively readily soluble oil with a rotation of 58 to 60° and a difference of from 4 to $5,3^\circ$ between the direct rotation and the rotation of the distillate¹⁾, and with a comparatively high citral-content (5 to $5,8$ p. c. according to Romeo²⁾, or $4,5$ to 5 p. c. according to the hydroxylamine method) is furnished by the East Coast of the Province of Messina especially by the districts of *St^a Teresa* and *Scaletta*.

A typical oil from volcanic districts has a rotation of $+61$ to 63° , the rotation of the distillate¹⁾ is about 5 to 7° less. It is less soluble and has a citral-content, according to the hydroxylamine method, of 4 to $4,2$ p. c. (according to Romeo $4,3$ to $4,5$ p. c.)²⁾. As the season grows older the citral-content increases, whereas the solubility remains almost unchanged.

An oil produced on chalky soil (*Syracuse*) showed a rotation of 65 to 67° , was readily soluble, had a normal (?) citral-content and showed only a slight difference between the direct rotation and the rotation of the distillate. (Oils with a high rotation scarcely ever show a larger difference than 3° .)

Estragon Oil. Our Miltitz plantations have furnished material for a sufficient supply of this oil. Our quality is very much sought after and our stocks therefore, as a rule, do not last long.

Eucalyptus Oil. Our globulus oil, containing over 80 p. c. of eucalyptol, has been in very strong demand during the last few months, because the reports received from Australia are to the effect that the producers are asking higher rates and that there is talk of an impending restriction of the manufacture. In spite of the fact that we hold large stocks of eucalyptus oil we have been compelled to advance the quotations several times, after first affording our customers an opportunity of covering their supplies in good time at advantageous rates. The market remains firm and we regard a further tightening of the prices as more than likely.

¹⁾ The author does not state whether the initial 10 p. c. or 50 p. c. of the distillate are referred to.

²⁾ We have already on a previous occasion, in discussing this method, pointed out that it gives no useful results. *Comp. Report* October 1905, 30.

The ordinary variety containing phellandrene, which we offer for sale under the collective name of Australian eucalyptus oil, has a firm tendency. At the present preposterously low prices the manufacture, it is said, is no longer profitable.

R. T. Baker and H. G. Smith¹⁾, the well-known authorities on the eucalyptus oils, have again described the following new distillates:—

Oil of *Eucalyptus acaciæformis*, Deane et Maiden. This species is known as "red" or "narrow leaved peppermint", and is widely distributed throughout N. S. Wales. The leaves yielded 0,197 p. c. of an oil which, in the crude state, possessed a brown colour and a turpentine-like odour: d_{150} 0,8864, $\alpha_D + 35,7^\circ$, n_{D20} 1,4713, insoluble in 10 vols. 80 p. c. alcohol. Its principal constituent is *d*-pinene, and it also contains the sesquiterpene of the eucalyptus oils (aromadendrene), and probably geranyl acetate.

Oil of *Eucalyptus Andrewsii*, J. H. Maiden. This eucalypt was formerly regarded as a variety (*Oxleyensis*) of *Eucalyptus Sieberiana*, but has been recognised by J. H. Maiden²⁾ as a separate species. The oil-yield amounted to 1,27 p. c. The leaves had been gathered in the N-E-part of N. S. Wales: d_{150} 0,8646, $\alpha_D - 41,5^\circ$, n_{D150} 1,4854, ester v. 4,3, insol. in 10 vols. 80 p. c. alcohol. The crude oil had a lemon-yellow colour. It consists principally of *l*-phellandrene (m. p. of the nitrite 105° and 112 to 113°), piperitone and sesquiterpene. Pinene does not appear to be present and cineol was scarcely traceable.

Oil of *Eucalyptus campanulata*, Baker et Smith. The leaves of this new species were obtained from the N-E-part of N. S. Wales. They yielded 0,851 p. c. oil. The colour of the crude product was pale yellow: d_{150} 0,8804, $\alpha_D - 25,8^\circ$, n_{D180} 1,4856, sap. v. 7,6, barely soluble in 10 vols. 80 p. c. alcohol. The following constituents were found present: phellandrene (principal constituent), cineol, piperitone and eudesmol.

Baker and Smith next refer to a few little known eucalyptus oils, which they have more closely investigated and to which we will here briefly refer:

Oil of *Eucalyptus Bridgesiana*³⁾. The yield amounted to 0,73 to 0,745 p. c. The constants of the oil were as follow: d_{150} 0,9223 to 0,9246, $\alpha_D + 1,9$ to $+1,8^\circ$, n_{D20} 1,4716 to 1,4729, sap. v. 8,7 and 7,6. The cineol-content was 73 and 78 p. c. (estimated by the phosphoric acid method). When purified by steam-distillation the data of the oil were as follow: d_{150} 0,9203, $\alpha_D + 3,1^\circ$, n_{D21} 1,4602.

Oil of *Eucalyptus laevopinea*⁴⁾. The crude oil was found to possess the following properties: d_{150} 0,8875 and 0,8871, $\alpha_D - 30,7$ to $33,3^\circ$, n_{D190} 1,4691 to 1,4697. It does not contain above 5 p. c. cineol.

¹⁾ Journ. and Proceed. Royal Soc. of N. S. W. 45 (1911), 267. From a copy kindly sent to us.

²⁾ A critical revision of the genus *Eucalyptus*, Vol. I, p. 195. Sydney 1909.

³⁾ Baker and Smith, A research on the *Eucalypts*. Sydney 1902, p. 86.

⁴⁾ Baker and Smith, *ibidem* p. 41.

Oil of *Eucalyptus dextropinea*¹⁾. The yield of crude oil was 1,02 p. c. d_{150} 0,8831, $\alpha_D + 24,2^\circ$, n_{D210} 1,4688, sap. v. 22,1, sol. in 10 vols. 80 p. c. alcohol. After being purified by steam distillation, the constants were as follow: d_{150} 0,8698, $\alpha_D + 24,4^\circ$, n_{D220} 1,4647. The product was nearly colourless. The crude oil contains 3,7 p. c. geranyl acetate.

Oil of *Eucalyptus nova-anglica*²⁾. The average properties of this oil are as follow: d_{150} 0,9221 to 0,9301, $\alpha_D + 0,9$ to $5,8^\circ$, n_{D150} 1,4892 and 1,4944 n_{D180} 1,4857, n_{D200} 1,4932, sap. v. 5,7 to 6,9. The cineol-content is very small, but sesquiterpene is present in considerable proportion. Phellandrene was occasionally found to occur in very small quantities.

Part 4 of the second volume of the work "A critical revision of the genus *Eucalyptus*", edited by J. H. Maiden³⁾, describes the following species of *Eucalyptus*: *Eucalyptus melliodora*, A. Cunn. (*E. cœrulescens*, Naudin) *E. fasciculosa*, F. v. M. (*E. paniculata*, Sm. var. *fasciculosa*, Benth.), *E. uncinata*, Turcz. (*E. leptophylla*, F. v. M.; *E. desertorum*, Naudin); *E. decipiens*, Endl. *E. concolor*, Schauer; *E. Cloëziana*, F. v. M. (*E. stannariensis*, Bailey; *E. Stuartiana*, Mac Mahon, non F. v. M.) and *E. oligantha*, Schauer.

Part 5 of the same volume contains a description of: *Eucalyptus oleosa*, F. v. M. (*E. socialis*, F. v. M.; *E. laurifolia*, Behr; *E. socialis*, F. v. M., var. *laurifolia*, F. v. M.; *E. turbinata*, Behr et F. v. M.) with the varieties *longicornis*, F. v. M. and *glauca*, Maiden; *E. Gillii*, Maiden (*E. socialis*, F. v. M., var. *laurifolia* part.; *E. laurifolia*, Behr part.) and *E. falcata*, Turcz. with the variety *ecostata*, Maiden.

Oil of *Eugenia Jambolana*. From the seeds (known as "Jambul seeds") of *Eugenia Jambolana*, Lam. (N. O. Myrtaceæ); a native of the East Indies, F. B. Power and T. Callan⁴⁾ have isolated 0,05 p. c. volatile oil, possessing the following constants: d_{200}^{200} 0,9258, $\alpha_D - 5^\circ 42'$. The oil was of a pale yellow colour and had an agreeable odour. Its b. p. lay between 145 and 155° (25 mm.)

Oil of *Euonymus atropurpureus*. From the root-bark of *Euonymus atropurpureus*, Jacq. (N. O. Celastrineæ), H. Rogerson⁵⁾ has obtained 0,01 p. c. essential oil with b. p. between 120 and 160° (25 mm.). The oil gave a pronounced reaction of furfural. When the oil was allowed to stand a body with m. p. 120° separated out of it, possibly furane- β -monocarboxylic acid.

Fennel Oil. According to such information concerning this year's crop in Galicia as was available up to the end of August, the prospects were not unfavourable, although the crop is late. More recently, however, disquieting news has come to hand, to the effect that heavy rains have

¹⁾ Baker and Smith, *A research on the Eucalypts*. Sydney 1902, p. 38.

²⁾ Baker and Smith, *ibidem* p. 34.

³⁾ See Report April 1912, 79.

⁴⁾ *Pharmaceutical Journ.* 88 (1912), 414.

⁵⁾ *Journ. chem. Soc.* 101 (1912), 1042.

seriously damaged the crop. A few weeks must yet elapse before the actual result of the harvest can be passed under review to some extent, and before the prices have found their level. The offers which are at present in the market are quite exceptionally high, but they are probably purely speculative, and their purpose apparently is to find out what attitude the consumers will take up towards them. The acceptance of these offers would be the signal for a rushing-up of prices, of which the end could not be foreseen.

On the oil-yield of *galbanum gum-resin* and the properties of the oil, see p. 24.

Geranium Oil. Unfortunately it is still impossible to make any cheerful reports with regard to African geranium oil. The scarcity to which allusion was made in our last *Report* has become much more pronounced still, and for pure quality it has been necessary to concede prices far exceeding 60 francs. As a result of this, business has naturally been restricted to the narrowest limits, and no one can be surprised that the consumers shrink from paying such figures and are casting about for substitutes. The exports of African geranium oil from Algiers in the first half of the year 1912 amounted to 13800 kilos, compared with 14300 kilos in the corresponding period of 1911. So far as we are in a position to judge, the supplies available in the producing country are very small indeed, and are hardly likely to hold out until the commencement of the second distilling season in October. As we have already pointed out on previous occasions, the memory of the losses suffered in previous years appears to be still so keen among the planters that they have lost all inclination to continue occupying themselves with geranium cultivation, notwithstanding the highly tempting character of the present range of quotations. By far the greater number of those who formerly grew geraniums have now taken up wine-growing.

The position of Réunion geranium oil has been exceedingly firm throughout the summer; in fact, the prices reached a point at which the employment of the oil as the basis of many important perfumes is rendered practically impossible. According to the reports which have reached us, sales have recently taken place at 70 francs, whereas in March of this year the quotation still stood at 42 francs. We must decline to express any opinion on the prospects of the market, especially because the fluctuations have lately been subject to factors which make all calculations impossible. We have touched repeatedly upon this matter in previous *Reports* and we can only repeat now that speculation continues to play an important part in the course of the prices. The exports of Réunion geranium oil from St. Denis in the first seven months of the present year show a decline on those for the corresponding period of 1911, having been 25614 kilos and 29103 kilos respectively.

In view of the exorbitant quotations for both varieties of geranium oils the problem naturally became of immediate interest of discovering a substitute which, at a moderate price, would as nearly as possible reproduce the effect of the odour of geranium oil. Almost without exception, the numerous substitutes which have been placed on the market under various fancy names by other firms have failed to fulfil the latter condition. It has therefore been to us a source of particular satisfaction to have been able to place upon the market, in the form of our Geranium Oil Substitute a product which, coupled with a very moderate price, answers all the requirements which consumers have a right to expect from a synthetic geranium oil of real usefulness. We will not omit here to call attention to this novelty, and we shall be glad, by furnishing samples, to enable our friends to form their own opinion of the article.

Ginger Oil. It has been very difficult during the last few months to procure raw material suitable for distilling purposes, hence the prices have kept at their former level. For the present there are no indications of any improvement in the position, and it will therefore be necessary to be prepared for a continuance of the high values. The market is certainly decidedly firm and those who now cover their requirements for the next few months may escape the necessity of having to pay considerably more afterwards.

The principal countries of production of the ginger which is consumed in Europe are the West Indies, India, Java, Japan and Sierra Leone¹⁾. The subjoined table shows the exports of ginger from Jamaica, Sierra Leone and India and the imports into the United Kingdom, Hamburg and Austria-Hungary: —

Exports from		1906	1907	1908	1909	1910
Sierra Leone ²⁾ . . .	Cwt.	11 584	12 369	12 733	14 438	21 866
	Value £	10 880	11 579	11 871	14 147	33 288
	Average price per cwt. . . £	0,94	0,936	0,932	0,98	1,52
Jamaica ³⁾	Cwt.	19 802	18 009	15 890	20 708	20 990
	Value £	27 722	39 620	46 289	44 071	37 188
	Average price per cwt. . . £	1,4	2,2	2,9	2,2	1,8
India ³⁾	Cwt.	88 118	48 353	49 368	64 649	65 544
	Value £	83 516	64 481	74 037	96 732	107 466
	Average price per cwt. . . £	0,95	1,3	1,5	1,5	1,64

¹⁾ Bull. Imp. Inst. 10 (1912), 118.

²⁾ To 31st December.

³⁾ To 31st March.

Imports into		1906	1907	1908	1909	1910
United Kingdom	Cwt.	37 243	26 709	38 612	40 923	42 939
	Value £	64 070	65 906	88 772	90 702	100 771
	Average price per cwt. £	1,72	2,47	2,3	2,22	2,35
Hamburg	Cwt.	4 522	6 422	12 748	10 583	11 883
	Value £	8 499	10 449	20 651	20 842	25 539
	Average price per cwt. £	1,88	1,63	1,61	1,97	2,15
Austria-Hungary	Cwt.	3 873	2 394	4 228	3 122	3 635
	Value £	7 500	4 292	10 333	7 792	9 853
	Average price per cwt. £	1,94	1,75	2,44	2,5	2,71

Gingergrass Oil. The demand for this oil has been very slack indeed, and it is therefore not surprising that at the coming of the new crop considerable quantities are left over from 1911, of which the cost-prices are very cheap. It will therefore be necessary for the producers in India, if they want to find any buyers for the article at all, to be very moderate in their demands. During the summer the prices have remained unchanged.

An instance of lævorotation observed in gingergrass oil has given occasion to W. H. Simmons¹⁾, to call attention to this alleged anomaly, which, he believed, had never before been observed. The oil in question, of which the properties otherwise were normal, had a rotation to the left of 21° , and, when more closely examined, proved to be unadulterated.

To this we may remark that in the course of years we have repeatedly handled lævorotatory gingergrass oils of guaranteed purity. Two such oils, with rotation $-19^\circ 12'$ and $-27^\circ 15'$ respectively have been referred to in a previous *Report* (April 1910, 85). As the author in his article *inter alia* appealed to our *Reports* we have availed ourselves of the opportunity to write to Mr. Simmons, calling his attention to these lævorotatory gingergrass oils described by us, and were informed that these references had escaped his attention because they appeared under the heading of "palmarosa oil".

It may be a matter of interest to many readers if we take this occasion to place on record the limits of value which, up to the present, have been observed by us in gingergrass oil: d_{15° 0,90 to 0,953, $\alpha_D + 54$ to -30° , $n_{D^{20^\circ}}$ 1,478 to 1,493, acid v. up to 6,2, ester v. 8 to 29, ester v. after acetyl. 120 to 200. The oils are often soluble in as little as from 2 to

¹⁾ *Perfum. and Essent. Oil Record* 3 (1912), 108.

3 vols. 70 p. c. alcohol; but when more alcohol is added opalescence to turbidity generally ensues; from 0,5 to 1,5 vols. 80 p. c. alcohol is sufficient to procure a solution; but here also, in a very few cases the dilute solution exhibits a slight opalescence. An oil which was recently examined in our laboratory gave the remarkably high ester value 54,5. For the rest it behaved normally (d_{150} 0,9403; α_D — $14^{\circ}34'$; n_{D200} 1,48373; ester v. after acetyl. 167,0). No adulteration with fatty oil or artificial esters could be detected. It follows from the above that in certain circumstances the ester value may attain the limit stated, provided always that the oil is not the product of another species of grass.

Hop Oil. The hop crop, which is now in progress everywhere, is very abundant and in all districts will be far in excess of that of 1911. There will therefore probably be at length an opportunity this year of again distilling hop oil, an article which for some considerable time has been entirely wanting. Consumers, however, have learnt to dispense with the oil, as is evident from the slight demand which was experienced last year. The world's production of hops in 1911 is estimated at 1808000 double centners (of 100 kilos); in 1911 it was 1365000 double centners. The world's average yearly consumption of hops is estimated by an authoritative source at 1780000 double centners.

On the occurrence of α - and β -caryophyllene in hop oil, see p. 149.

Hyssop Oil. We again have at our disposal a sufficient quantity of an exquisite distillate produced from plants of our own growing.

Juniper Berry Oil. Exact information with regard to the result of the crop in the different producing districts is not yet available, but from Italy, which probably supplies the bulk of the juniper berries used in the German essential oil industry, comes the report that this year's yield is even smaller than was that of 1911, which itself was insufficient to meet the requirements. In 1911, however, large quantities of berries from the year 1910 were available. As a result of the news referred to above there has already been an advance of about 10 p. c. in the price of Italian berries. No particulars are yet to hand with regard to the Hungarian crop, but we hear from Italy that operators there are trying to buy Hungarian berries, the outlook being unfavourable. It will not be possible to form a precise opinion of the market-position until after the course of a few weeks, but it may already be said that lower prices than those now prevailing can certainly not be looked for.

Cyprian Juniper Berry Oil. We received from the Imperial Institute in London a sample of juniper berry oil distilled in Cyprus, which we will here describe briefly, as it represents a novelty in respect of the place

of origin. The oil was of an extremely faint pale-yellow colour, and in its odour reminded not so much of juniper berry oil as of pumilio oil. It possessed the following constants: d_{15}^0 0,8688, $\alpha_D +3^\circ 41'$, n_{D20}^0 1,47210, acid v. 0,6, ester v. 10,2, sol. in 8 vols. & m. 90 p. c. alcohol, with slight cloudiness.

From the dextrorotation of the oil it may perhaps be concluded that, in addition to juniper berries, juniper needles have also been worked up in the distilling, because, for example, Russian juniper oils from similar raw material, which were sent to us several years ago, were also dextro-rotatory¹⁾. This may also perhaps explain the peculiar odour of the Cyprian distillate, which must militate against its employment as juniper berry oil.

Ladanum Oil. From a paper by E. J. Emmanuel²⁾ on Cretan Ladanum oil (from *Cistus creticus*, L.) we take the following particulars relating to the essential oil which was separated from the product. For the purpose of preparing the oil the ladanum resin was first extracted with ether; the ethereal extract was freed from acid by repeated shaking with soda solution, and finally washed with distilled water. The ether was then distilled off and the residue, after the addition of a 3 p. c. sodium hydroxide solution, was treated with steam. This process yielded a pale-brown oil with a pleasant odour of ladanum-camphor. The oil-yield equalled 2 p. c. of the ladanum used. The oil boiled at 225° and had sp. gr. 0,928, $n_{D12,50}^0$ 1,5118.

Upon continuing the steam distillation some colourless crystals passed over. They possessed a faint aromatic odour and had m. p. 89° ; they were insoluble in water, soluble in methyl and ethyl alcohol, readily soluble in ether, chloroform, and acetone. From the determination of the molecular weight and the result of combustion, Emmanuel concludes the formula to be $C_{17}H_{30}O$. He gives to this compound the name of Ladaniol, but leaves it in doubt whether it really represents a new body or whether the substance is identical with the "Champacol" which was described by Merck years ago (1893).

In connection with this matter Emmanuel also refers to guajol, which was first isolated by us³⁾ from guaiacum wood. He appears to be of opinion that Merck's Champacol and our guajol represent different bodies, although their identity has been pointed out both by ourselves⁴⁾ and by Wallach⁵⁾. Moreover, Wallach has shown that the formula $C_{17}H_{30}O$, assigned to Champacol by Merck is incorrect, the true formula being $C_{15}H_{26}O$. As, at the time, the firm of Merck was not dealing with champaca oil (as they believed to be the case), but with guaiacum wood oil¹⁾, the

¹⁾ Comp. Report April 1907, 60.

²⁾ Arch. der Pharm. 250 (1912), 111.

³⁾ Report April 1892, 56.

⁴⁾ Report April 1893, 42.

⁵⁾ Liebigs Annalen 270 (1894), 395.

designation "Champacol" of the body in question is without any real foundation; on the contrary, the only proper designation is that of guajol. Emmanuel's ladaniol, it would seem, corresponds with the last-named body.

Lagam Oil. Up to the present it has been held that one of the constituents of lagam oil was a sesquiterpene of which the hydrochloride had m. p. 114° ¹⁾, but only recently an investigation conducted by L. van Itallie and M. Kerbosch²⁾ has disclosed further particulars with regard to the constitution of the oil. These authors examined two kinds of lagam balsam, one liquid, the other of elemi-like consistency. The liquid variety, alleged to be derived from *Canarium eupteron*, Miq. (N. O. Amyridaceæ) appears in fact to be the product of a dipterocarp. The liquid balsam contained 49 p. c. colourless essential oil, which was found to possess the following constants: $d_{15}^{15^{\circ}} 0,9051$, $\alpha_D - 7,5^{\circ}$, $n_{D24^{\circ}} 1,4972$. More than 93 p. c. passed over between 258 and 261° ; the rectified oil possessed the following properties: b. p. 261 to 263° , $d_{15}^{15^{\circ}} 0,905$, $\alpha_D - 7,46^{\circ}$, $n_{D16,5^{\circ}} 1,49935$. These constants led to the assumption that the oil consisted of caryophyllene; but as a matter of fact it yielded both the caryophyllene alcohol (m. p. 92 to 94°) and the blue nitrosite, m. p. 111 to 112° .

The solid variety of lagam balsam is derived from *Dipterocarpus Hasseltii*, Bl. or from *D. trinervis*, Bl., two closely allied, and possibly identical, dipterocarps. By steam-distillation the authors obtained from this balsam 10,5 to 22 p. c. essential oil, possessing the following constants: $d_{15}^{15^{\circ}} 0,9065$, $\alpha_D - 8,9^{\circ}$, $n_{D16,5^{\circ}} 1,50029$. This oil also consisted of caryophyllene (m. p. of the nitrosite 112 to 113°).

Larch Turpentine Oil, see Turpentine Oil, p. 111.

Lavender Oil. The forecast with respect to this article given in our last *Report* has been realised; throughout the summer the prices have been well maintained. All parcels of really good quality had passed into firm hands as early as the spring and for inferior qualities also the producers were able to command very stiff rates indeed. The favourable prospects for the present year's crop might possibly have contributed to a weakening of the market during the summer, for the reports were thoroughly favourable, but only small stocks remained to meet the fairly sustained demand and everybody interested was looking forward eagerly to the arrival of the new oil. Distilling commenced under favourable auspices, but rain and cool weather set in shortly afterwards, and as a result of these conditions the oil-yield turned out to be poor. The producers were only too ready to take advantage of these circumstances to show a firmer front, the more so because certain buyers, without any apparent reason, paid such inflated prices for the new flowers that the

¹⁾ Haussner, *Arch. der Pharm.* **221** (1883), 245.

²⁾ *Ibidem* **250** (1912), 199.

collectors and producers suddenly had their heads completely turned. We on our part naturally refused to take part in such an unjustifiable upward rush of prices and immediately suspended all our purchases of flowers. This action proved immediately successful; the producers adopted a more reasonable attitude, and we were able to secure the bulk of our raw material at prices of which the average at least compared favourably with those paid by our competitors. Our factory at Barrême, which had been enlarged in the course of the year by the installation of a new boiler and the doubling of the distilling plant¹), was working at full pressure night and day during the distilling season; the total quantity of lavender flowers worked-up there amounting to 510 000 kilos. In addition to these we distilled 180 000 kilos in the works leased by us at Sault (Dep. Vaucluse); 190 000 kilos in our itinerant stills at Castellane, Vergons, Thoard and Clamensane, and about 45 000 kilos in small stills in various other localities. The total quantity distilled by us therefore reached in the present year the important figure of about 900 000 kilos of lavender flowers. It is hardly necessary to say that no other firm engaged in the distillation of lavender oil reaches figures like these.

It may be imagined that such a result has not been attained without exciting envy, as is shown by an anonymous article signed "Un Montagnard" ("A Dweller in the Hills") which appeared in the *Revue de Grasse* of June 23rd. The author reproaches us with paying enormously high rents for lavender fields which are the property of the State or the Communes, and he advises the authorities who control these properties to let them to us on the longest possible leases, so that the department of Forests and the Communes may profit as much as possible from the fancy prices which we are alleged to pay, and which, he says, could not otherwise be maintained in the long run. We should like in the first place to point out to the author that he is ill-informed, for we assume as a matter of course that he does not deliberately distort the facts. For instance, in Annot not two lettings took place, as stated by him, but only one, and this was knocked down to one of our confidential agents for 1000 fcs. In previous years it had realised 725 fcs., not 250 fcs. as asserted by him. The increased price paid by us for the present year has been justified at once by the increased yield of the crop, estimated at between 30 and 40 p.c., but we may further point out that a firm in Grasse, through its confidential agent, paid for a lease at Le Fugeret 400 fcs., and for one at Méailles 710 fcs., the rent paid in 1911 for the first of these leases having been only 70 fcs., and for the second only 155 fcs. In other words, the increased rent amounted in the one case to 471 p.c. and in the other to 358 p.c., while for the land leased by us in the Commune of Annot we paid barely 38 p. c. more than it fetched in 1911. The land at Sault,

¹) An illustration will be found in this *Report*.

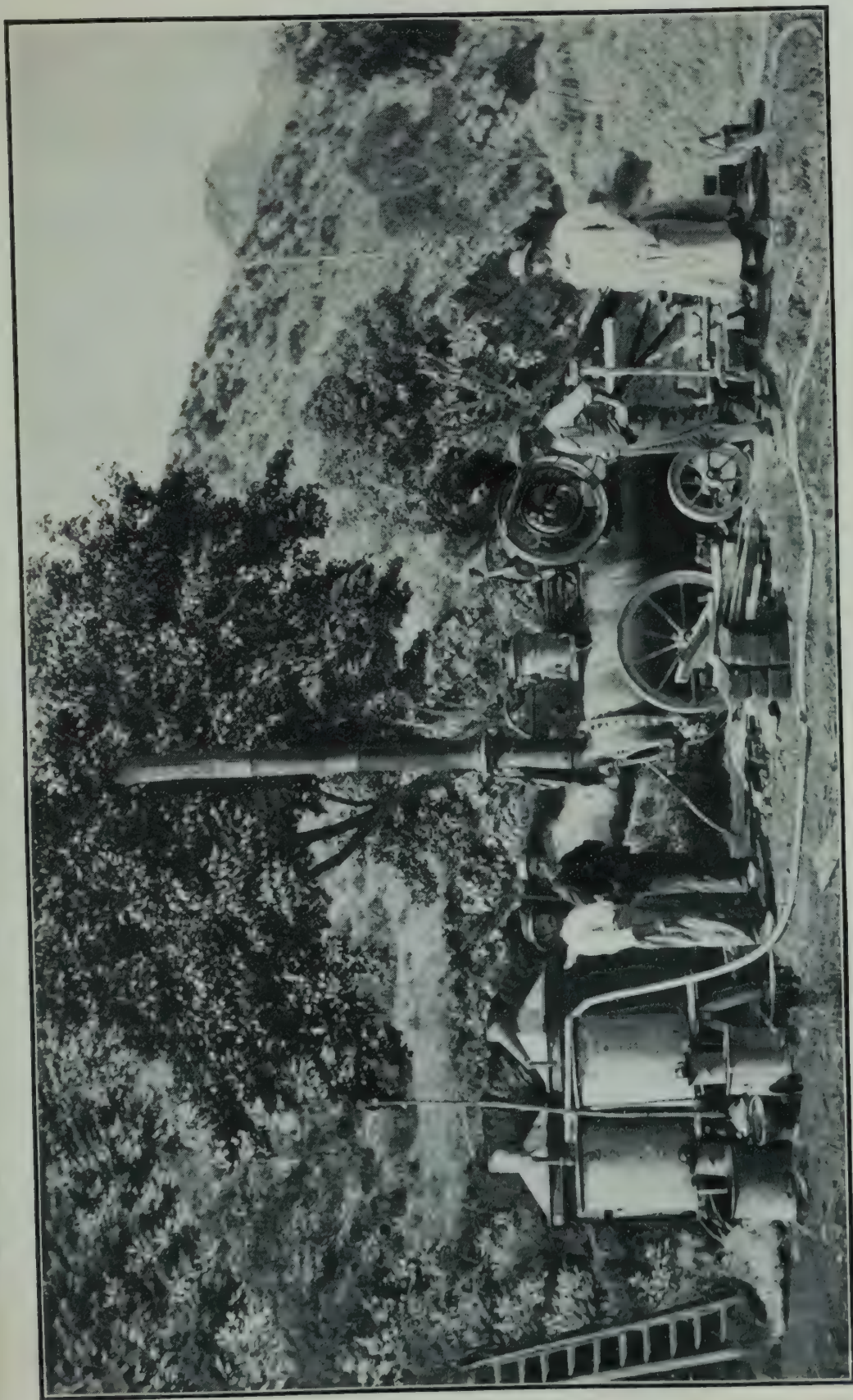
where we were also represented, and which consisted of the slopes of Mont Ventoux, was let this year for 2000 fcs., against 660 fcs. in 1911. Another plot, which had previously been let for 460 fcs. was knocked down for 1540 fcs. It goes without saying that in all these instances we abstained from making any bids whatsoever, because we perceived that our competitors were deliberately rushing up the prices. "Un Montagnard" therefore accuses us unjustly of driving up the prices, for, as we have shown above, the land secured by us was leased at by far the most favourable terms secured by any lessor. His reproaches should be taken to heart by those of his countrymen who showed themselves so open-handed without any logical ground. In the same article the writer urges the distillers to prepare an oil of superior quality to ours by using cultivated lavender flowers, but in doing so he ignores the fact that we have for some time been the owners of lavender-plantations, and we may here lead him into the secret that it is our intention considerably to extend these plantations in the future. We hope that we shall thus, in the course of time, be in a position to supply the requirements of our Barrême work entirely from our own plantations. In passing, we may observe that we distil at Barrême between 25 000 and 28 000 kilos of lavender flowers daily.

As stated at the commencement of this article, we only paid for a very short time the high prices which, in spite of the favourable prospects, were conceded to the collectors at the beginning of the season. In the end these prices reached a figure of 20 fcs. per 100 kilos, but we fixed our buying-rates in the district of Barrême and in other localities where we employ buyers, at 12 fcs. Although it would be thought that in these circumstances the purveyors of flowers would have taken the whole of their merchandise to our competitors and left us in the lurch, it soon turned out that after all they were unable to dispose elsewhere of their large supplies, and from that time forward we found no difficulty in acquiring the bulk of our requirements of flowers at reasonable rates. We may congratulate the manufacturer who has shown the good taste to entice the flower-purveyors away from us on our own threshold so to speak, by offering them fancy prices, upon the brilliancy of his conception and not less so upon the "cheap" cost-price of his lavender oil!

"Un Montagnard" will probably be very little pleased with the critical review of his article by an expert which has recently appeared in the *Seifensiederzeitung*¹⁾, and which we cannot omit to publish *verbatim* here in order to complete the account of the incident. This criticism is as follows:—

Great interest attaches to an article which appears in No. 25 of "*La Revue de Grasse et le Commerce*" of June 23rd 1912. In this article it is specially pointed out that the German firm of Schimmel & Co. of Leipzig has again attempted this year to buy up, as far as possible

¹⁾ *Seifensieder Ztg.* 25 (1912); 744.



Schimmel & Co.'s itinerant Lavender distillery at Castellane.



all the lavender flowers and all the lavender oil obtainable at high prices, higher at least than those which the French firms are prepared to concede. It is said that owing to this policy the bulk of this important essential oil during the last 3 or 4 years has passed into the hands of foreigners, without any attempt being made to put a stop to such proceedings. As an example, it is reported that this year the firm in question paid 1000 fcs. for two plots of lavender land for which last year only 200 fcs. was paid. By this means the firm in question is said to be building up a dangerous monopoly which will hand over the industry of Grasse to the mercies of the German chemists.

As a result thereof, some mild outcry is being raised for State assistance, but at the same time it is recognised that the State could only do very little in the matter. It is also difficult to make any serious reproaches to the owners of the lavender-plantations, and the critics therefore content themselves to prophesy all sorts of future ills for these owners because, it is said, it is certain that the prices cannot remain at the present level.

As a counter-stroke, the Communes are advised to cultivate under their own management, and on a large scale, a particularly good variety of lavender plants, to produce locally an oil of a quality much superior to that now produced, and then to leave the other planters, including the firm of Schimmel, to get rid of their inferior oil as best they may. It is said that such plantations are already conducted elsewhere with the greatest possible success, and that therefore the result is, so to say, guaranteed.

It is also admitted that the demand is far in excess of the production, that good results are obtainable with good qualities, and that it is therefore unnecessary to labour literally *pour le roi de Prusse* ("working for the King of Prussia" is a French colloquialism for working for nothing).

Now, when we look a little at these assertions through a magnifying glass, they really amount to nothing else than to an acknowledgment of the alertness of the firm of Schimmel, inasmuch as the policy of that firm really leads to the improvement of the lavender plantations, just as it has been mainly due to that firm that a strict eye has been kept on the dealers in lavender oil, who used to adulterate their wares in a truly shameless manner. Even firms of some importance used not to be above foisting upon their old and large customers in Germany, and probably also in other countries, lavender oil which had been doctored to the largest possible extent, for it is quite well known in France that even among the largest perfumery manufacturers in Germany there are very few indeed whose laboratories are equal to the task of examining analytically the oils supplied to them. This made such practices, which are a gross abuse of confidence, all the more reprehensible. Who, therefore, can blame German firms if they try to secure as large a quantity of pure oil as possible direct from the producers, or if they purchase the plants from the growers in order to distil them themselves and thus to be in a position to offer their clients a guaranteed pure article? Similarly, we shall be sincerely grateful to those French Communes who will cultivate a finer quality of lavender plants on their fields, and thereby enable us to buy from them a better oil than in the past, an oil which is not inferior in purity to the other kinds which are offered, while surpassing it in

delicacy. This, in fact, is all that the Germans are trying to bring about, and it may be assumed that the other side are quite well aware of the fact, although the object is represented under another guise. The German perfumery manufacturers, and no doubt the manufacturers in other countries also, will be delighted if they are offered a better quality of merchandise than formerly and no doubt they will be quite prepared to pay higher prices for such a quality than they have paid in the past for normal oil. The whole article in the paper in question almost makes the impression as if the great days of adulterated oil belong to the past, and as if therefore it is impossible to urge too strongly the extension of the plantations. If this is so, the German firms, or the "German Chemists", could have rendered no service worthy of greater thanks. But is it likely that this point of view and this possibility have been present in the mind of "Un Montagnard"? Well, hardly!

But the article also admits of another inference, namely that the reason for the present exorbitantly high price of lavender oil may be found in the fact that really pure oil is not to be had in the market at present, and that the lavender oils which were offered so plentifully for some time, were actually all adulterated.

Since the article quoted above appeared, we have seen a contribution on the subject in the journal *La Parfumerie Moderne*¹⁾, of which the following is a translation:—

The foreign distilling-plants in France. — The firm of Schimmel & Co. of Leipzig has put up a new chimney at its factory in Barrême. This chimney is a significant symbol, which our French distillers will often behold in their dreams as if it were a menace

It is worthy of note that the same firm has leased at the enormous rental of 1000 francs each two small communal fields at Annot, fields which in previous years no one would look at for 200 francs or even less. A foreign firm has carried the bidding for the lease of a lavender field belonging to the Commune of Gréolières, which last year realised 250 francs, up to 1222 francs. Finally, however, this field was knocked down to a Frenchman, M. Beilet of Le Bar.

These figures indicate excellent prices. Especially when the Germans referred to, who distil very little oil in their own factory, which is really a decorative one, are anxious to buy as fast as they can and at increased prices, for those blockheads who pay 10 francs per kilo more for an oil which is alleged to have been distilled in a German factory . . .

And then it is expected that Frenchmen should be found childish enough to pay more than the market-price for these alleged perfected oils

These spiteful allegations far exceed the limits of the permissible according to what is held becoming in this country, and we do not intend to honour the writer with a reply. His assertions, moreover, are sufficiently disproved by the explanations which we have given above, and for the rest we leave it to our readers to form their own opinion of this attack.

¹⁾ *Parfum. moderne* 8 (1912), 98.

For some considerable time attempts have been made to cultivate essential-oil yielding plants in the State of Victoria, but so far with very little success. We gather, however, from an article by J. Knight¹), that quite recently the prospects have improved. Knight is of opinion that lavender can be grown successfully by the rural population. The grower, however, should be content to sell either the flowers or the oil, and should not attempt to manipulate the oil in the making-up of perfumes, as all such attempts have hitherto only led to failure. In the neighbourhood of Melbourne about 40 lbs. of oil per acre has been produced, and in Pentridge an acre yielded from 3 to 4 tons of flowers.

In the subjoined table we present a comparison of several samples of lavender oil which have been submitted for our opinion in the course of the past six months, and the examination of which revealed in every instance an increase of the original ester-content by the addition of foreign esters (mostly glycerol acetate). In order to afford a clearer review we have indicated those values which deviate from the constants of normal oils by heavy type. We deem it desirable once more to point out the absolute necessity of carrying out, in the case of all oils which are valued according to their ester-content, the test for foreign esters proposed by us, for a glance at the table shows that several of the samples possessed quite normal constants, although nevertheless a more thorough examination showed them to be adulterated.

In samples Nos. 1 and 2, fractional saponification of the original as well as of the steam-distilled oil showed excessive difference between the ester-value estimated in concentrated and that estimated in dilute solution (comp. *Report* October 1911, 116) an addition in each oil of about 3 p. c. terpinyl acetate being thereby established.

Sample No. 3 was similarly adulterated, but in addition the presence in this sample of an ester of a sparingly-volatile acid and of a certain proportion of glycerol acetate was established. (For the estimation of acid v. II comp. *Report* October 1910, 61; for the detection of glycerol ester *Report* April 1911, 150, and the present *Report*, p. 60, under bergamot oil.)

All the other samples likewise contained glycerol ester: — In the case of sample No. 8, which apparently contained 54,1 p. c. linalyl acetate, we should have liked to have had at our disposal a larger quantity of experimental material, for we should then have been able to expose the impudence with which the sophisticators proceed in order to impart to inferior oils an apparent ester-content which surpasses even the actual ester-content of our speciality of high-grade Barrême lavender oil.

¹) *Journal of Agriculture*, Victoria, May 1912. Quoted from *Chemist and Druggist* 81 (1912), 369.

	No. 1		2		3		4		5		6		7		8	
Lavender oil	Original oil		Steam-dist.		Original oil		Steam-dist.		Original oil		Shaken 3 times with 5 p. c. alc.		Original oil		Shaken 3 times with 5 p. c. alc.	
αd ₅₀	0,8899	—	0,8976	—	0,9025	—	0,8990	0,8953	0,8946	—	0,8966	0,8946	0,8933	0,8887	0,9011	0,8980
α _D	—60°17'	—	—60°11'	—	—49°15'	—	—49°22'	—70°11'	—70°11'	—	—60°45'	—	—60°35'	—	—20°54'	—
Sol. in 70 p. c. alcohol	2,5 vols. 8 m.	—	2,5 vols. 8 m.	—	2,2 vols. 8 m.	—	—	2,5 vols. 8 m.	2,5 vols. 8 m.	—	2 vols. 8 m.	—	2 vols. 8 m.	—	2 vols. 8 m.	1,8 vols. 8 m.
Acid v.	0,5	—	0,5	0,5	0,8	0,6	0,5	0,5	0	0,5	0,5	0,5	0,5	0,5	0,5	0,6
Ester v. after 1 h. sap. ¹⁾ with 10 cc. seminormal lye	93,5	—	114,7	115,1	92,9	84,8	80,3	105,4	93,3	108,9	102,4	100,8	89,4	65,0	60,1	154,5
Ester content (calc. as finalyl acet.)	32,7%	—	40,1%	40,3%	32,4%	29,7%	28,1%	36,9%	32,7%	38,1%	35,8%	35,3%	31,3%	22,7%	21,0%	54,1%
Ester v. after 2 h. sap. with 20 cc. seminormal lye	96,8	98,9	117,3	117,2	95,9	—	86,0	107,1	—	109,2	—	101,7	—	—	63,3	—
Ester v. after 1 h. sap. with 10 cc. seminormal lye + 25 cc. alcohol	88,6	88,5	109,7	109,1	86,9	—	73,1	103,7	—	106,3	—	99,3	—	—	58,8	—
Difference	8,2	10,4	7,6	8,1	9,0	—	11,9	3,4	—	2,9	—	2,4	—	—	4,5	—
Sap. v.	94,0	—	115,2	—	93,6	—	80,8	105,9	—	109,4	—	101,3	—	—	65,5	—
Acid v. II	88,4	—	111,7	—	80,9	—	72,8	104,2	—	107,4	—	99,8	—	—	61,5	—
Difference	5,6	—	3,5	—	12,7	—	8,0	1,7	—	2,0	—	1,5	—	—	4,0	—
Terpinyl acetate content, about	30%	—	30%	—	30%	—	—	not traceable	not traceable	not traceable	not traceable	not traceable	not traceable	not traceable	—	—
Esters of sparingly volatile acids	not traceable	—	not traceable	—	present	—	—	not traceable	not traceable	not traceable	not traceable	not traceable	not traceable	not traceable	—	—
Glycerol ester, seminormal lye for 10 cc. filtrate	not traceable	—	not traceable	—	1,2 cc.	—	—	1,3 cc.	—	1,45 cc.	—	1,73 cc.	—	0,75 cc.	—	—
Ester separated off	—	—	—	—	—	1,40%	—	—	1,40%	—	—	1,50%	—	—	—	5,02 cc.
Sap. v.	—	—	—	—	—	521,3	—	—	605,7	—	605,9	—	567,4	—	—	—

¹⁾ With oils which are very rich in ester 15 or 30 cc. seminormal potash liquor should be used; also comp. Report April 1912, 85 and 86.

Normal
Lavender oil

0,882 to 0,896
—3 to —9°
Sol. in 2 to 3 v. 8 m. 70 p. c. alcohol. High perc. oils are possibly more sparingly sol.

at least 30 p. c.

Diff. so far observed in fract. sap. up to 4.

Diff. between sap. v. and acid v. II so far observed up to 3.

Lawang Oil. A bark imported from the Dutch Indies under the name of "Lawang", has been examined by E. W. Mann¹⁾. It yielded 0,5 p. c. of an oil with an odour reminding of mace, sassafras and cloves and possessing the following constants: $d_{15.50}$ 1,0104, α_{D20} —6,97°, n_{D20} 1,5095, acid v. 1,15, ester v. 41,87, sap. v. after acetyl. 121,91, sol. in 2 vols. 80 p. c. alcohol. When heated with metallic sodium the oil reacted violently, producing a semi-solid mass. This mass was extracted with ether, when a substance was dissolved out which turned blue on exposure to air. The portion which is insoluble in ether is readily soluble in water. When the aqueous solution was acidulated a white body was precipitated from it which, when recrystallised from alcohol, had m. p. 51 to 52°. So far the nature of this compound has not been disclosed.

Mann is unable to give any particulars concerning the botanical origin of the bark. He only states that Holmes is of opinion that it is probably derived from a *Cinnamomum*- or *Litsea*-species.

We surmise this suggestion to be correct, for according to de Clercq²⁾ *Lawang* is the Malay name for *Cinnamomum iners*, Reinw.; N. O. Lauracæ. The leaves and bark are used in the Dutch Indies as a medicament, and the bark also as a spice.

Lemongrass Oil. The trade in this article, which is one of such great importance for the perfume industry, has shown a considerable expansion in the period between July 1st 1911 and June 30th 1912. During those 12 months the shipments from Cochin were as follows:—

to London	1000 cases, against	820 cases in the previous year,						
„ Hâvre	1393	„ „	1666	„	„	„	„	„
„ Marseilles	5284	„ „	2212	„	„	„	„	„
„ Bremen	316	„ „	250	„	„	„	„	„
„ Hamburg	1170	„ „	1003	„	„	„	„	„
„ New York	1164	„ „	285	„	„	„	„	„

Total: 10327 cases, against 6236 cases in the previous year.

During the spring of the present year the price was at first maintained at about 4¹/₂ d. per oz., but as the new crop approached it receded to 3¹/₂ d., at which considerable transactions for shipment took place. The market then showed a temporary improvement, but lately a listless tone has again set in, from which it may be concluded that the output this year will be considerable. The increase of the shipments to Marseilles is remarkable, that port being now far ahead of all other markets. France and Switzerland, the last-named country in particular, consume far more than one-half of all the arrivals in the manufacture of synthetic violet perfumes.

¹⁾ *Pharmaceutical Journ.* 89 (1912), 145.

²⁾ *Nieuw Plantkundig Woordenboek voor Nederlandsch-Indië.* Amsterdam 1909, p. 199.

Limette Oil. This article has been characterised by great scarcity throughout the summer and it has repeatedly been necessary to raise the quotations. We have very little stock left and are most anxiously expecting fresh supplies. Our purveyor informs us that the crop has been gravely injured by exceptional drought and that this has had the effect of very greatly reducing the production for the present.

Linaloe Oil. The only thing which can be reported concerning this article is that Mexican linaloe oil has generally been firm throughout the summer, and has maintained its previous value. The supplies were just sufficient to meet the not very heavy demand, hence there has been no accumulation of stocks in Hamburg, the principal centre for the article. The large supplies of Cayenne linaloe oil in second hand, of which the cost-price was far below the values of Mexican oil, have impeded the sale of the last-named variety. But the brisk sale of linalol and linalyl acetate, the odoriferous substances prepared from linaloe oil, has lately caused a great part of these second-hand supplies to be cleared off, and as according to the reports from Cayenne there does not seem to be any prospect that the oil produced in that colony will again recede to its old price-level, it is probable that sooner or later interest in the Mexican oil will revive. The present quotation in Cayenne is 27 to 29 fcs., compared with 19 fcs. at the beginning of the year. It is said that at the old prices distilling does not pay, and now that a number of former producers have been forced to leave the distilling-business in the hands of a few well-to-do firms, the latter are of course trying all they can to keep the market, if possible, from falling below the present level. We are doubtful, however, whether they will long succeed in keeping it there.

As long ago as the year 1908 we isolated in our laboratory from Mexican and also from Cayenne linaloe oil a body possessing the formula $C_{10}H_{18}O_2$, which even at that time, on account of its constants and other properties, we set down as an oxide of linalool. After the publication of a paper by N. Prileschaeff¹⁾ on the oxidation products of unsaturated compounds, in which among others a linalool monoxide is mentioned, we were able (as will be seen from what follows) to show that the body $C_{10}H_{18}O_2$ was identical with the linalool monoxide of the author in question. Prileschaeff quotes the following data for the oxide prepared from linalool: b. p. 95° (25 mm.), $d_{16}^{16^\circ} 0,9507$, $\alpha_D - 4,98^\circ$, $n_{D16^\circ} 1,4554$, mol. refr. found 48,59, calc. for $C_{10}H_{18}O_2$ 48,842. It is said that upon hydration the oxide yields, in the place of a glycol, a doubly unsaturated aldehyde, b. p. 120 to 122° (25 mm.) with a semicarbazone melting at $138,5^\circ$.

The following physical constants were ascertained by us at the time for preparations derived from linaloe oil:—

¹⁾ *Berl. Berichte* 42 (1910), 4811; comp. *Report April 1910*, 154.

B. p. 193 to 194°, 63 to 65° (4 mm.), d_{150} 0,9442, $\alpha_D - 5^\circ 25'$, n_{D20} 1,45191,
Mol.-Refr. $C_{10}H_{18}O_2$ 48,78 calc. 48,88;

B. p. 193 to 194°, 71 to 73,5° (6 to 7 mm.), d_{150} 0,9431, $\alpha_D - 5^\circ 46'$,
 n_{D20} 1,45221.

Combustion:

1. 0,1795 g. subst.: 0,4652 g. CO_2 , 0,1721 g. H_2O .
2. 0,1597 g. subst.: 0,4114 g. CO_2 , 0,1531 g. H_2O .
3. 0,1642 g. subst.: 0,4250 g. CO_2 , 0,1583 g. H_2O .

	Found			Calc.	
	1.	2.	3.	f. $C_{10}H_{18}O_2$	f. $C_{10}H_{18}O$
C	70,68	70,26	70,58 p. c.	70,60	77,92 p. c.
H	10,65	10,45	10,71 p. c.	10,65	11,69 p. c.

The body is somewhat viscous and is also clearly differentiated from linalool by its mouldy odour, which reminds somewhat of fenchyl alcohol and of camphor. As its b. p. is only 3 to 4° lower than that of linalool, it is impossible, in view of the very small extent to which it occurs in the oil, to prepare it in the pure form by fractionation. It is however possible to obtain it in this form, although at a considerable loss of material, by repeatedly oxidising the fractions containing linalool of high sp. gr. with 0,5 p.c. permanganate solution under ice-cooling, each time driving off the unattacked oil with steam. It also appears to be possible to accumulate the compound by treating the fractions in question with glacial acetic-sulphuric acid at 40 to 50° for several hours. It was ascertained at the time, from the formation of esters, that the body $C_{10}H_{18}O_2$ represents an alcohol. Its acetic ester, of which the odour differs altogether from that of linalyl acetate, boils between 60 and 65° (4 mm.), its benzoic ester between 157 and 160° (3 to 4 mm.). When treated with other reagents, such as phenylisocyanate, diphenyl carbamic chloride, phthalic anhydride, semicarbazide, and bromine, no solid derivatives were obtained. As an oxidation-product, first with permanganate and subsequently with bichromate and sulphuric acid, the body yielded acetone (m. p. of the bromophenylhydrazone, 92 to 94°) and in addition to acetic acid, an oily acid which was possibly identical with lævulic acid.

For purposes of comparison we have prepared the linalool oxide according to Prileschaeff's method by oxidation of linalool with benzoyl hydrogen peroxide and have obtained preparations possessing the following constants, which agree with those of the natural product.

d_{150}	α_D	n_{D20}	b. p.
0,9450	$-4^\circ 6'$	1,45231	55 to 56° (3 mm.)
0,9449	$-4^\circ 51'$	—	—
0,9443	$-4^\circ 46'$	—	—
0,9441	$-5^\circ 41'$	1,45403	—

The odour of the synthetic product is exactly like that of the oxide isolated from linaloe oil and also resembles the latter in its other

present we are still unable to give an explanation of this peculiarity observed by us, but in any case the fact has to be taken into account that it is possible, in certain circumstances, for linaloe oils of good quality to have a somewhat higher linalyl acetate content.

Matico Oil. Now that our stocks are exhausted we are regretfully compelled to abstain from quoting this oil for the present, as we cannot succeed in procuring suitable raw material. The shipments of matico leaves to Europe have lately fallen off very considerably.

Melaleuca Oils. Continuing their investigations of the Australian *Melaleuca*-species¹⁾, R. T. Baker and H. G. Smith²⁾ have discovered that cajuput oil (of *Melaleuca Leucadendron*, L., N. O. Myrtaceæ) is not a typical representative of the melaleuca oils. The oils which they now describe deviate considerably from cajuput oil in their constitution.

Oil of *Melaleuca genistifolia*, Sm. According to an old statement by Bosisto, this plant yields 0,07 p. c. oil. Baker and Smith, however, obtained from leaves and terminal branchlets collected on the coast of N. S. Wales, 0,526 p. c. of an oil of pale yellow colour, with a well-defined odour of turpentine, possessing the following constants: d_{150} 0,8807, $\alpha_D + 32,7^\circ$, n_{D220} 1,4702, sap. v. 6,8, insol. in 10 vols. 80 p. c. alcohol. A fraction, b. p. 154 to 158° was found to contain *d*- α -pinene (nitrosochloride m. p. 104°); a portion boiling between 162 and 183° contained 2 p. c. cineol (resorcin method). The highest-boiling fractions contain a sesquiterpene. The oil contains from 80 to 90 p. c. pinene.

Oil of *Melaleuca gibbosa*, Labill. The distilling material consisted of leaves and terminal branchlets collected in Tasmania. The oil-yield was 0,158 p. c.; the crude oil was deep-yellow and had an odour of cineol and pinene: d_{150} 0,9138, $\alpha_D + 4,5^\circ$, n_{D200} 1,4703, sap. v. 9,9, insoluble in 10 vol. 70 p. c., soluble in its own vol. 80 p. c. alcohol. The oil contained 61,5 p. c. cineol (estimated by the resorcinol method). Another important constituent is α -pinene (m. p. of the nitrosochloride 104°) while the highest-boiling fractions contain a sesquiterpene and perhaps also terpinyl acetate.

Oil of *Melaleuca pauciflora*, Turcz. The distillation-material was derived from the Coast of N. S. Wales (leaves and terminal branchlets). It yielded 0,3 p. c. of an oil of a dark amber colour and somewhat viscous consistency, possessing the following characters: d_{150} 0,9302, $\alpha_D + 3,3^\circ$, n_{D240} 1,4921, sap. v. 8,25, barely soluble in 10 vols. 80 p. c. alcohol. The oil only contains 8,7 p. c. cineol (estimated by the resorcinol method). Another sample of the oil gave the following constants: d_{150} 0,9552, n_{D240} 1,4923. No pinene was found present, but the oil may contain limonene or dipentene. It is possible also that it contains terpinyl acetate as well as about 5 p. c.

¹⁾ Comp. Report April 1907, 14; November 1908, 28; April 1912, 93.

²⁾ Journ. and Proceed. Royal Soc. of N. S. W. 45 (1911), 365. From a copy kindly sent to us.

free terpineol. As much as 67 p. c. of the oil passed over between 260 and 270°. The principal constituent appears to be a sesquiterpene. The product which boils between 260 and 270° and possessed the following constants: $d_{15} 0,9364$, $\alpha_D + 8,5^\circ$, $n_{D21} 1,5004$. It gives characteristic colour reactions with glacial acetic acid and sulphuric acid (red coloration), with acetanhydride and sulphuric acid (green coloration) and with bromine vapour (blue coloration). When left to stand the last-named colour change by way of violet into green. It would appear that this sesquiterpene occurs in the high-boiling fractions of many melaleuca oils.

Milfoil Oil is again available in sufficient quantities, but we have been obliged to raise the prices very materially. The collectors of the raw material, both here and in the neighbourhood of our Bodenbach works, demanded much higher rates than formerly, and in the end we were forced to concede their demands as otherwise we could not have made any oil at all.

Monarda Oils. An investigation by Nellie Wakeman on the different *Monarda*-species is referred to on p. 142.

Mustard Oil. The demand for our distillate of oil from mustard seed has not been particularly animated, for as we have already pointed out on previous occasions, the use of oil from seed has fallen off materially. Synthetic mustard oil having to a large extent replaced the natural article.

It is well-known that we are manufacturers of the synthetic oil on the very largest scale, and the only reason why we have occasionally refused to follow the low prices of competitors is that we have had difficulty in finding a market for our output at full rates.

The results of the investigations into the determination of mustard oil in mustard seed which have been carried out by D. Raquet¹⁾ go to establish the advantage of alcoholic over aqueous maceration. In a flask of 250 cc. capacity, Raquet places 5 grams powdered mustard-meal with 100 cc. water and 20 cc. 90 p. c. alcohol. The flask is then closed and heated during one hour to from 30 to 35°, or it is left to stand for 6 hours with frequent shaking. Distilling is then proceeded with from a glycerol-bath, the distillate being caught in a flask of 100 cc. capacity, containing 10 cc. ammonia ($d_{15} 0,925$). After about 50 cc. has distilled over, the distillate is diluted with 20 cc. decinormal silver solution and the distilling-process is continued, after shaking, until a volume of 100 cc. has been obtained. The mixture is now heated for one hour to 80 to 85° with reflux, filled up after cooling, and filtered through chlorine-free paper. 50 cc. of the distillate is titrated as usual with decinormal ammonium sulphocyanide solution. If N = the number of cc. used up, and $10 - N$ = the number

¹⁾ *Ann. Chim. analyt. appl.* **17** (1912), 174. Quoted from *Chem. Zentralbl.* **1912**, II. 4

cc. decinormal silver solution, then $(10 - N) \cdot 0,198 =$ the quantity of allyl-isosulphocyanate yielded by 100 grams mustard flour.

By this method, English mustard seed was found to contain 1,386 p. c.; Greek 1,198 p. c.; mustard seed from Merville 1,08 p. c.; Sicilian 0,99 p. c.; Bari mustard seed 0,99 p. c. and Bombay mustard seed 0,81 p. c. allyl-isosulphocyanate.

H. Pénau¹⁾ has likewise been engaged in the determination of allyl-isosulphocyanate in preparations of mustard. He rejects the usual methods of weighing the sulphide of silver which has been separated out, or of titrating the excess of silver solution with ammonium sulphocyanide according to Volhard. In lieu thereof he proposes either to weigh in the form of chloride of silver the silver which has not entered into reaction, or to titrate it with decinormal silver solution after adding an excess of cyanide of potash.

From a paper by C. Grimme²⁾ on the fatty oils of the Cruciferæ we take the subjoined table showing the volatile oil-content of the various mustard-seeds. The estimation was carried out according to the prescription of the German Pharmacopœia V. for the estimation of the mustard oil content of black mustard seed.

No.	Name	P. c. of Mustard Oil in the	
		Press Residue	Seed
1	<i>Brassica oleracea acephala vulgaris</i>	0,119	0,079
2	" " " <i>quercifolia</i>	0,079	0,051
3	" " " <i>crispa</i>	0,159	0,103
4	" " <i>gemmifera</i>	0,198	0,144
5	" " <i>sabanda</i>	0,178	0,129
6	" " <i>capitala alba</i>	0,357	0,258
7	" " " <i>rubra</i>	0,357	0,259
8	" " <i>gongylides</i>	0,198	0,142
9	" " <i>botrytis</i>	0,159	0,104
10	" " <i>asparagoides</i>	0,178	0,119
11	" <i>Rapa oleifera annua</i>	0,119	0,085
12	" " " <i>hiemalis</i>	0,159	0,093
13	" " <i>rapifera</i>	0,252	0,166
14	" " <i>teltoviensis</i>	0,198	0,132
15	" <i>Napus oleifera annua</i>	0,156	0,097
16	" " " <i>hiemalis</i>	0,119	0,071
17	" " " <i>flora alba</i>	0,099	0,056
18	" " <i>rapifera</i> ("Erdkohlraabi")	0,099	0,062
19	" " " ("Wruke")	0,020	0,012
20	<i>Raphanus sativus albus</i>	0,263	0,164
21	" " <i>niger</i>	0,179	0,108
22	" " <i>Radiola</i>	0,159	0,106
23	" " <i>oleiferus</i>	0,199	0,133

¹⁾ Journ. de Pharm. et Chim. VII. 6 (1912), 160.

²⁾ Pharm. Zentralh. 53 (1912), 733. Pharm. Ztg. 57 (1912), 520

Neroli Oil. We had already announced in our last *Report* that the price of the present year's distillate would be about 400 fcs. This estimate has proved to be correct, for although the crop in respect of quantity has not been quite equal to that of 1911, and owing to the cool weather during the distilling season the oil-yield left a great deal to be desired, the *Société Coopérative* fixed the prices of flowers at 70 to 75 centimes per kilo probably because it was thought that a higher figure might adversely affect the demand. In spite of this, the *Société* only succeeded in disposing of 1 100 000 kilos of flowers and was therefore compelled this season, as on previous occasions, to distil the remainder itself. 800 000 kilos flowers produced about 760 kilos of neroli oil which, taken with the balance left over from last season, form a very considerable quantity and are hardly likely to be saleable without some sacrifice. Hence the tendency of the market has been weak, although it was only here and there that oil was offered at less than 400 fcs. and in such cases it was mostly admixed with petitgrain oil, or with linaloe and bergamot oil, distilled over orange flowers.

In former years most of the perfumery manufacturers were wont to follow with some uneasiness the price-fluctuations of this costly and important oil, but the introduction upon the market of our artificial neroli oil has suddenly freed them from all care in this matter, for it was very soon recognised that it was impossible to over-estimate the advantages of this cheap substitute. We have laboured without cessation to perfect the quality and we strongly advise those of our friends who have up to the present assumed a sceptical attitude towards this exquisite perfume to convince themselves by practice that our repeated and perhaps apparently somewhat high-flown recommendations of our artificial neroli oil are thoroughly justified.

Nigella Oil. The beautiful blue fluorescence of the oil of *Nigella damascena*, L. (N. O. Ranunculaceæ) is due to the presence of an alkaloid, damascenine, tho the synthesis of which by A. J. Ewins we have already referred briefly in our last *Report*, p. 96. Since that time, Ewins¹⁾ has described the results of his investigations of damascenine in greater detail and we are therefore able to amplify our previous references by the following data: 50 g. *m*-hydroxybenzoic acid were dissolved in 200 cc. methyl alcohol and a solution of 30 g. sodium hydroxide in a minimum quantity of water was added. The mixture was then treated with 90 g. methyl sulphate, with which it reacted vigorously. The reaction was mitigated by the addition of 50 p. c. aqueous potash solution. 60 grams of methyl sulphate were then added in small quantities alternately with the solution of potassium hydroxide. From the aqueous liquid *m*-methoxybenzoic acid separates out upon the addition of hydrochloric acid. M. p. 107 to 108°.

¹⁾ *Journ. chem. Soc.* **101** (1912), 544.

When nitrated, the acid yields a mixture of nitro-derivatives from which 2-nitro-3-methoxybenzoic acid (m. p. 249 to 250°) may be separated out without difficulty. When reduced this acid is converted into 2-amino-3-methoxybenzoic acid, of which the hydrochloride has m. p. 204 to 205°. The free acid, when heated with methyl iodide in a sealed tube at 100°, yields the hydriodide of 2-methylamino-3-methoxybenzoic acid. This is converted into the corresponding hydrochloride (m. p. 210 to 211°) by warming with freshly-precipitated silver chloride; this hydrochloride being identical with that of damasceninic acid. Passing hydrogen chloride into the methyl alcoholic solution of the hydrochloride gives rise to the hydrochloride of a methyl ester, from which latter, by the splitting-off of hydrochloric acid, methyl-2-methylamino-3-methoxybenzoate = damascenine (m. p. 23 to 24°) is formed. When mixed with the natural product, the synthetic damascenine suffers no depression of m. p. The hydrochloride of damascenine has m. p. 156°, the picrate, 158 to 159°. The result of these investigations has shown that the formula $C_9H_{11}NO_3$, assigned to the alkaloid by Pommerehne¹⁾ is incorrect, while the formula $C_{10}H_{15}NO_3$, which was assumed by Schneider²⁾, almost corresponds with the actuality. The so-called methyl damascenine which has been isolated from the seed of *Nigella aristata* by Pommerehne and Keller³⁾ is identical with damascenine.

Nutmeg Oil. Nutmegs of qualities suitable for distilling have occasionally been very scarce, but thanks to our important stocks of cheap oil we have so far been able to avoid raising our prices. It is difficult to forecast the future of the article, the market being entirely dependent upon the consignments which are sent for auction to Amsterdam and the course of prices being subject to the general tendency of the spice-market, which is influenced by quite a number of factors. In any case the present position must be described as firm.

Oil of Ocotea (*Mespilodaphne*) pretiosa. A paper by G. Laloue on oil of *Mespilodaphne* (*Ocotea*) *pretiosa*, Nees, which has recently appeared in the *Bulletin de la Société chimique* [IV. 11 (1912), 602], and which had previously been published, in October 1910, in the *Berichte* of Roure-Bertrand Fils, was referred to in our *Report* of April 1911, p. 83.

Origanum Oil. The distillation and sale of origanum oil in the island of Cyprus, which have been carried on for over 10 years by the Department of Agriculture there, will in the future be taken up by a private distiller. The quantity of oil produced in the year 1910 amounted to 2842 lbs.⁴⁾

¹⁾ *Arch. der Pharm.* **238** (1900), 546; **239** (1901), 34. *Comp. Report* April 1901, 42.

²⁾ *Pharm. Zentralh.* **31** (1890), 173, 191.

³⁾ *Arch. der Pharm.* **246** (1908), 1. *Report* April 1908, 73.

⁴⁾ *Bull. Imp. Inst.* **10** (1912), 148.

Orris Oil. We have received from our local informants the following report on the Florentine orris root market: —

In our report on Florentine orris root of last March we pointed out that the stock then available had been reduced to about 120 tons. It is many years since the supply had shrunk to such small dimensions and this circumstance is no doubt a leading factor contributing to the increased firmness of the market and to the consequent advance of prices, which led to the sale of the last lots of available root in July of the present year at 115 lire on the spot, a figure equalling 95 marks per 100 kilos cif. Hamburg. At the end of July no orris root whatever was obtainable in the various producing centres of Tuscany while the warehouses in Florence and Leghorn held only insignificant quantities, which were likewise cleared before the end of August. The pretensions of the producers were supported by this total lack of old supplies and they therefore had no difficulty in advancing the quotations for orris root of the new crop. These prices were partly fixed even before the digging of the root, on the basis of the average grass-yield. The producers asked from 30 to 35 lire per 100 kilos grass basis, but such prices are prohibitive, seeing that they would represent a parity of over 120 lire per 100 kilos for the dry root, ready for delivery in the producing centre. — During the past month it was generally believed that the new plants were vigorous and promising and this was the advice given to us by our confidential agents who had inspected the several growing districts. We were therefore justified in assuming that the crop would be a good one, both in respect of quantity and of quality. We called the producers' attention to these facts, and succeeded in causing them to abate their absurd demands and to take up a more sensible attitude. At the present time the work of peeling (trimming) the new root is already well advanced, and our anticipations so far as quality is concerned have turned out in the main to be well-founded, the root being generally fine and healthy. But the quantity of the output has been considerably affected by a disease of which the cause is as yet unknown, but which also frequently attacks the vines and olive-trees and destroys their fruit. It is therefore pretty safe to say that the output of trimmed root ready for the market will be less than was originally expected. The average yield was at first estimated at about 700 tons, whereas it is now thought that the total production will not surpass 600 tons and we ourselves are of opinion that the last-named figure will hardly be reached. At the end of August of last year the stock of orris root of the old crop amounted to between 90 and 100 tons, while the new crop yielded rather more than 600 tons; from which it follows that the total available quantity this year will be at least 100 tons less than last. Taking into the account, apart from the reduction in the available supply, the fact that between March of this year and the present time only unimportant parcels have been bought for export and that consequently the stocks abroad must be either exhausted or greatly reduced, it is to be expected that before long there will be a keen demand on the part of foreign buyers for covering their requirements. At the present moment, owing to lack of buying-interest, the market is rather flatter, but as soon as the inevitable demand from abroad sets in the prices will at once begin to advance, and owing to the reduced quantities which will be available for the next twelve months we fail to see how the prices can possibly fall, either now or later.

The exports during the past 10 years have been as follows:—

September 1902 to	August 1903	840 Tons,
" 1903 "	" 1904	820 "
" 1904 "	" 1905	500 "
" 1905 "	" 1906	920 "
" 1906 "	" 1907	550 "
" 1907 "	" 1908	525 "
" 1908 "	" 1909	755 "
" 1909 "	" 1910	760 "
" 1910 "	" 1911	560 "
" 1911 "	" 1912	690 "
		Total: 6920 Tons.

The average of the season, therefore, has been 690 tons. Seeing that at the close of the season 1911/12 the whole of the old stock had been cleared, it follows that with a crop estimated to reach not quite 600 tons, there will be a shortage of about 100 tons in the average quantity required for shipment.

Basing ourselves upon our many years' experience of the article, and upon the data concerning the new crop which are at our disposal, we regard any important fluctuations in the prices of orris root this season as impossible.

We have been obliged recently again to advance the prices of both our qualities of orris oil, after first giving our regular customers an opportunity of covering their requirements at the old rates. The cheap stocks of orris root are now at an end, and the sustained demand has caused the prospects of the future course of the market to become much firmer.

We would take this opportunity of giving a word of commendation to our Orris-Resinoid, which is much esteemed in the manufacture of toilet soap as a perfume-fixing agent.

Palmarosa Oil. The position of this article must be described as extremely quiet. This is probably in the first place a consequence of the fact that owing to the high prices of the last few years the employment of substitutes, such as our Palmarosa Oil Substitute, has been resorted to in many quarters, and because those who have once taken the step are loath to abandon this cheap and efficient preparation. During the summer there have been no fluctuations whatever in the prices of palmarosa oil, but the market must be called weak, for transactions of any importance have been completely wanting, although the stocks in India have been exhausted since about the month of May. Nothing definite is yet heard about the new crop. In the principal districts distilling commences in the month of October. The scanty offers which have come to hand thus far mentioned high prices, but they were probably altogether of a speculative character, for in view of the favourable course of the monsoon (see introduction, p. 10) there does not appear to us to be any logical ground for regarding the future of the article with a pessimistic eye.

Parsley Oil. There has been a great scarcity of oil distilled from parsley seed (an article which is often asked for in France), because it has been very difficult to procure the necessary raw material, last year's crop having turned out a failure. It has been necessary to make a corresponding advance in the prices.

We desire to call special attention to our parsley oil distilled from fresh leaves, which is coming more and more into use in the industry of comestibles. We distil this oil from parsley grown here in Miltitz and we can thoroughly recommend it for use in the preparation of soups, seasonings, meat-extracts, condiments, &c., as well as generally for use in the preserved provision industry.

Parsnip Oil, Italian. Roure-Bertrand Fils¹⁾ give the following constants of a sample of an Italian parsnip oil, distilled from the entire plant (yield 0,1 p. c.): d_{150} 0,8970, $\alpha_D + 0^\circ 6'$, acid v. 5,6, sap. v. 228,9 ester v. after acet. 251,1, sol. in 2 vols. & m. 80 p. c. alcohol. When more alcohol was added a considerable proportion of a paraffin was separated out.

Patchouly Oil. The half-yearly period now under review has again failed to bring with it the expected increase in prices, although high rates continued to be asked for patchouly leaves. It happens, however, that most consumers had laid in ample supplies at the time when prices were still cheap, the more readily so because patchouly is one of the few essential oils of which the aroma distinctly improves with prolonged storage. These heavy stocks of oil in the hands of our industry are naturally depressing the market, and as the offers of raw material have lately been on a somewhat more liberal scale, we regard it as probable that the increased prices of patchouly leaves of the past twelve months will not be reflected in the oil-quotations at all. There have been no arrivals of any importance of patchouly oil distilled in India.

Pennyroyal Oil. Although the demand for this oil has lately been very slack, a rather firmer tone has become perceptible in the market. The drought in the producing centres has greatly reduced the yield of this year's crop, and a further improvement in the prices in the course of the winter therefore appears likely. But in order to bring this about it must be assumed that the consumers will adopt a less reserved attitude towards the article.

Peppermint Oil, American. No price-alterations of importance occurred during the spring, and it was only when the prospects of the present year's crop became clearer, and it was possible to count with some degree of certainty upon a favourable yield, that the market began to show a corresponding easiness. The decline in prices, however, was to some extent balanced by the exceeding briskness of the demand,

¹⁾ *Berichte von Roure-Bertrand Fils, April 1912, 28.*

especially from the European markets, and as a result the quotations have lately acquired a certain stability. We are inclined to think that during the winter the prices of first-class qualities will not fall below those to which we reduced our oils in the middle of August.

In the course of the year our New York branch has again made a careful survey of the producing centres in the States of Michigan and Indiana; — Wayne County has notoriously ceased to be a factor in the estimation. We take from the report of our friends the following particulars concerning the area under cultivation this year: —

Michigan:	1911 acres	1912 this year's plants	1912 total	1911 oil in farmers' hands
Van Buren County	1405	490	1687	—
Cass "	1380	352	1525	5100
Saginaw "	1250	150	1350	—
Allegan "	1022	405	1258	3700
Berrien "	647	548	1120	—
Eaton "	485	181	355	1900
Kalamazoo "	328	136	413	2500
Montcalm "	231	177	365	—
St. Joseph "	428	196	350	900
Branch "	151	68	145	2300
Muskegon "	65	15	75	—
Total	7392 acres	2718 acres	8643 acres	16400 lbs.

Indiana:	1911 acres	1912 this year's plants	1912 total	1911 oil in farmers' hands
St. Joseph County and neighbourhood	2845	1422	3375	2700
La Grange County	838	366	1011	—
Noble "	200	40	150	—
Steuben "	100	10	50	—
Total	3983 acres	1838 acres	4586 acres	2700 lbs.

It appears from the above that the increased area under peppermint is compared with 1911 amounts to 1854 acres and that 4556 acres have been newly planted. Our expert estimates the total peppermint oil output for the present year at about 325 000 lbs., or about 40 000 lbs. more than that of 1911. The total stocks of last year's oil amount to 23 000 lbs., hence the world's requirements for the year are amply covered by the available quantities¹⁾.

Peppermint Oil, English. The reports on the probable yield of oil during the present year, which were at first very favourable, and which induced us to make a commensurate reduction in our prices, have unfortunately since then been replaced by most pessimistic news from the

¹⁾ Unfortunately, while this *Report* was in preparation, we received the news that owing to the badness of the weather during recent weeks the yield will fall far short of the expectations and that sellers have withdrawn from the market. The prices are therefore again beginning to show a very strong tendency.

Mitcham district, in which prices as high as last year's are talked of. Although at the time when this *Report* was in preparation the position of the market had not become sufficiently certain to call forth firm offers, it was evident that pure crude oil would not be purchasable for less than 30 to 32/- per lb. According to some reports, in fact, the harvest is said to be the worst for many years. Dry weather in April and May impeded the planting-out, and the few new plantations developed very badly. Cold weather in June caused rust, which compelled a great many planters to cut their peppermint as early as the third week in July to prevent total loss of the crop. Since the end of July rain has fallen almost daily; in the Mitcham district there were only 4 rainless days out of 36. It is not surprising that under such weather-conditions the plants should have suffered severely, and even if the autumn should turn out fine the situation would not be improved thereby. Nor are the conditions any more favourable in the peppermint districts of Lincolnshire, which have recently been afflicted by such heavy floods that all hopes have been dashed to the ground.

Peppermint Oil, Japanese. Since the spring there has been a not inconsiderable change in the market for Japanese peppermint products, and our prophecy that higher prices would be seen in the course of the summer has turned out entirely well-founded. The total crop of the year 1911, which is said to have amounted to about 320 000 kin, to which about 20 000 kin of 1910 product had to be added, was completely sold out in Japan at the beginning of July, and all accounts now agree that the yield of the first cutting in Bingo Bitchiu, which takes place in the months of July and August, will approximately represent the entire supply in the producing district. Generally speaking, firms in Europe, at least in our branch of business, appear to have bought favourably, for during the last few months a number of firms have been offering recrystallised menthol at prices far below the market-rates for crude menthol, and these cheap offers have only been withdrawn quite recently. Naturally, the Japanese are holding back in order to take the utmost advantage of the high prices for the present and also for the new crop, which, as will be seen below, promises to be abundant.

For these reasons we regard it as probable that the market will show increased stringency, at any rate until January, and we even believe that up to that time materially higher prices may be prognosticated, both for peppermint oil and for menthol. In January the bulk of the crop, consisting of the oil produced in Hokkaido, is usually brought to market, and it is not impossible that the position may then veer round. Of course, opinions on this subject vary, and there is no lack of reports which hold out prospects of an earlier reduction in prices. It is thought that if, owing to high cost of rice, there should be a great increase in the prices of necessities in Japan, the farmers might easily be led to abandon their fi-

attitude before the proper time in order to secure ready cash. Naturally also, climatic disturbances such as have occurred more than once in the past may upset all calculations. The probable reduction in values in January, if it should occur, will at first find only partial expression in the European market, because the cheap kinds cannot arrive here until the end of February or the beginning of March.

The estimate of the crop, which we present under reserve, is as follows:—

1st cutting Bingo Bitchiu (July/August)	about 30000 kin
2nd " " " (Sept./Oct.)	" 100000 "
3rd " " " (November)	" 100000 "
Yamagata (October)	" 15000 "
Hokkaido (January)	200 to 250000 "
Total 445000 kin	
to 495000 "	

These figures show an increase in 1912 over 1911 of from 30 to 40 p. c., indicating a very prolific crop.

Peppermint Oil, Saxon. The production this season has again been very small, owing to the climatic conditions having been throughout unfavourable to the development of the plants. The greater portion of our new distillate is already sold.

From investigations by F. Pilz¹⁾ it would appear that the peppermint plant requires a considerable supply of potash, but is less exacting in the matter of phosphoric acid. The leaves are richer in lime, phosphoric acid, and nitrogen than are the stalks, but both leaves and stalks contain almost the same proportions of soda and potash.

Petitgrain Oil, Paraguay. It is true that the political disturbances in Paraguay are not yet over and that prospects of a suppression of the revolution seem to be slight, but owing to the admirable energy displayed by our purveyors we have succeeded in securing a few small parcels, for which the consumers on this side were most anxiously waiting. It is not surprising that the price has risen to about 48 marks per kilo. Recently offers of oil for future delivery have come to hand from various quarters, which seems to indicate that in spite of the uncertain political conditions arrangements have been made to start the manufacture of the oil once more, at any rate in some quarters. For the present it will certainly be necessary to be prepared for high prices, and until the condition of Paraguay has improved a resumption of supplies on the old scale is not to be looked for.

¹⁾ *Zeitschr. f. landw. Versuchswesen in Österreich* 15 (1912), 575. Quoted from *Chem. Zentralbl.* 1912, II. 743.

The complaints which have made themselves heard of late years with regard to the deficient ester-content of petitgrain oil¹⁾ appear to have resulted in unscrupulous suppliers attempting to make good this deficiency by the addition of terpinyl acetate, a practice which so far we had not observed in the case of petitgrain oil. Lately two samples of oil thus adulterated have been examined in our laboratory, and in the subjoined table we quote these, together with two other oils which had also been sophisticated, but in a different manner.

Of the two samples which had been doctored with terpinyl acetate (Nos. 1 and 2) the first shows a somewhat excessive specific gravity, but for the rest it gives, as does No. 2, the analytical values of pure petitgrain oils, and only fractional saponification made it possible to conclude that it was adulterated. As the oils, when rectified with steam, showed as great differences as did the original oils, the addition of the ester in question was established. As determined by us from mixtures of known composition (comp. *Report* October 1911, 116) this addition amounted from 9 to 12 p. c. An attempt to separate, by fractional distillation *vacuo*, the terpinyl acetate from 1 kilo of sample No. 2, in which the addition was readily ascertainable from the odour, was unfortunately not attended by the desired result, because at a pressure of 3 to 4 mm. the boiling points of terpinyl acetate and of the esters which are naturally present in petitgrain oil lie very closely together. Hence even repeated fractionation was only able to establish the fact that the fractions in question had been enriched with terpinyl acetate, although the addition was considerable.

The sample mentioned under No. 3 possessed normal constants, and upon fractional saponification it showed a difference which was only slightly greater than in normal oils, but on the other hand the difference between acid v. II and the saponification value was 8,9, which indicated adulteration with an ester of a sparingly-volatile acid. Further examination established the fact that the oil contained several per cent. of a fatty acid, for after distillation with steam the saponification value and the acid value II agreed, from which it followed that the non-volatile acid must have been contained in the distillation-residue in the form of an ester. This residue of 5,7 p. c. was liquid, insoluble in alcohol, and had sap. v. 172,2.

Sample No. 4 was obviously also adulterated, inasmuch as its opt. rot. (—12°) was altogether abnormal, its ester content was only 29,4 p. c. and it was insoluble in alcohol or less than 90 p. c. But the quantity of oil submitted to us was too small to permit of a more thorough investigation, and it was therefore impossible to establish the cause of these abnormalities.

Pimento Oil has been maintained in price, for there have been but few opportunities of securing cheap and suitable raw material.

¹⁾ *Report* October 1910, 106.

Petitgrain oil	No. 1				2				3				4				Normal Petitgrain oil
	Original oil	Distilled with steam	Original oil	Distilled with steam	Original oil	Distilled with steam	Original oil	Distilled with steam	Original oil	Distilled with steam	Original oil	Distilled with steam	Original oil	Distilled with steam	Original oil	Distilled with steam	
d_{150}	0,9019	—	0,8968	—	0,8917	—	0,8905	—	0,886 to 0,900	—	0,8905	—	0,886 to 0,900	—	0,8905	—	
α_D	+4° 47'	—	+1° 40'	—	+2° 56'	—	—12° 0'	—	+5 to —4°	—	—12° 0'	—	+5 to —4°	—	—12° 0'	—	
Solubility	5 vols. & m. 70 p. c. alc. dilute sol. opal. 2,3	3 vols. & m. 70 p. c. alc.	3 vols. & m. 70 p. c. alc.	—	1 vols. & m. 80 p. c. alc. dilute sol. opal. 0,5	—	Any vol. 90 p. c. alc.	—	Generally in 2 to 4 vols. 70 p. c. alcohol, but fre- quently with opalescence to clouding.	—	Any vol. 90 p. c. alc.	—	Generally in 2 to 4 vols. 70 p. c. alcohol, but fre- quently with opalescence to clouding.	—	Any vol. 90 p. c. alc.	—	
Acid v.	111,2	115,1	112,4	113,3	136,8	113,3	137,5	84,0									
Ester v. after 1 h. sap. with 10 cc. seminormal liquor ¹⁾	38,9 p.c.	40,3 p.c.	39,4 p.c.	39,7 p.c.	47,9 p.c.	48,1 p.c.	29,4 p.c.	At least 37 p.c.									
Ester content (calc. as linalyl acetate)	119,3	121,8	121,8	126,1	138,5	139,3	85,1										
Ester v. after 2 h. sap. with 20 cc. seminormal liquor	102,3	106,0	99,7	103,0	133,5	133,0	82,9										
Ester v. after 1 h. sap. with 10 cc. seminormal liquor + 25 cc. alc.	17,0	15,8	22,1	23,1	5,0	6,3	2,2										
Difference	113,5	—	112,7	—	137,3	137,5	—										
Sap. v.	107,6	—	112,4	—	128,4	137,9	—										
Acid. v. II.	5,9	—	0,3	—	8,9	0	—										
Difference	9 p.c.	—	12 p.c.	—	not traceable	not traceable	—										
Terpinyl acetate content about .	not traceable	—	not traceable	—	present	—	—										
Ester of sparingly-sol. acids . .	not traceable	—	not traceable	—	not traceable	—	—										
Glycerol ester	—	—	—	—	—	—	—										
Distillation-residue	—	—	—	—	—	—	—										
Sap. v. of residue	—	—	—	—	—	—	—										

¹⁾ With oils which are very rich in ester 15 or 30 cc. semi-normal liquor should be used; also comp. Report April 1912, 85 and 86.

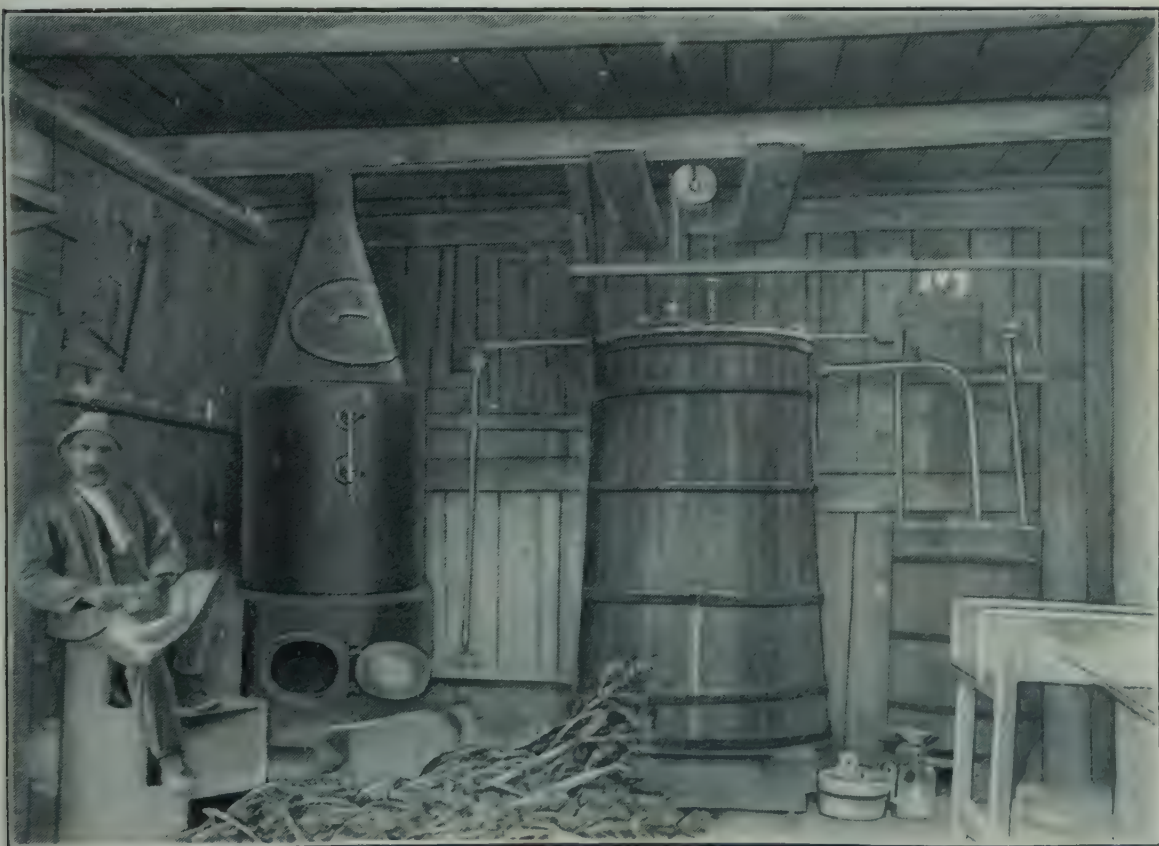
Pine-needle Oils. The popular Siberian pine-needle oil was plentifully available, but so much interest was shown for the large parcels which were offered from Russia that it was ultimately necessary to pay higher prices. This has caused the market to take a firm tone, which will probably grow still more pronounced in the course of the winter months, when no fresh supplies can be expected from Siberia. For this reason we cannot too strongly advise our customers to make their contracts now, so as to avoid having to pay higher prices in the end, as they may have to do if they hesitate too long.

The supply of oil from the cones of *Abies pectinata* (*Ol. templiniana*) has remained plentiful, and we have even been able to reduce our prices somewhat. It has been possible up to the present to procure sufficient quantities of oil from *Pinus Pumilio*¹⁾ at unchanged prices, but it is not unlikely that the scarcity which is already talked about will be much longer delayed, because in some parts the needful raw material is no longer obtainable and several districts have consequently ceased to produce. We understand that a scheme is being mooted for taking up distilling on a large scale in Transylvania, but in view of the want of success in other parts of Austria-Hungary there appears to be a good deal of difficulty in interesting experts in the project, although on its merits it would seem to hold out prospects of success.

There has been an abundant supply of oil from *Abies pectinata* from Lower Austria and the Black Forest, and the position of this article therefore does not call for remark. The field for its employment has been much enlarged by the various "air purifiers" and appliances for spraying perfume in rooms which are now on the market.

Oil from the seeds of *Abies pectinata*. The receipt of a small parcel of seed from *Abies pectinata* afforded us an opportunity of distilling this product by itself, whereas ordinarily the seed is worked up together with the cones. As the cones owe their oil principally to the seed which is enclosed in them, it was to be expected that the oil yield from the seed alone would be very high and that the distillate would completely agree, as regards characters, with the ordinary oil from cones. Both these anticipations were realised, but it was necessary to crush the seeds before placing them in the still, as otherwise not one-fifth of the oil contained in them would be recovered. For whereas the seed when whole only yields 2,3 p. c. oil, the crushed seeds yielded from 12 to 13 p. c. As already stated, the constants were those of the oil from cones and, in our distillates, ranged within the following limits: $d_{150} 0,8629$ to $0,8668$, $\alpha_D - 68^\circ 14'$ to $-76^\circ 38'$, $n_{D20} 1,476$ to $1,47812$, acid v. 0,5 to 1,8, ester v. 0,9 to 3,7 corresponding to 0,3

¹⁾ This Report contains two illustrations showing the production of *Pinus Pumilio* oil in the Tyrol.



Distillation of Pine-needle oil (*Pinus pumilio*) in Tyrol.

3 p. c. bornyl acetate; sol. in 5 to 7 vols. and more of 90 p. c. alcohol. In the seed of *Abies pectinata* the oil is located between the skin and the kernel.

Oil of Poplar Buds. We are now in a position to amplify our statements of a few years ago (*Report* November 1908, 103) on the constants of oil of poplar buds by the results of some further observations on two distillates of our own manufacture. The first sample (I) was distilled in our Bodenbach works, the second (II) in our works at Miltitz.

	Colour	$d_{15^{\circ}}$	n_D^{20}	Acid v.	Ester v.	Ester v. after acet.	Soluble in	
I	Pale yellow	0,8906	+ 6° 2'	1,49668	1,9	7,5	18,0	5 vols. 95 p. c. alcohol with separation of paraffin.
II	Light brown	0,9035	+ 3° 54'	1,49623	11,3	13,4	53,0	7 to 8 vols. 90 p. c. al- cohol with sep. of paraffin. 1 vol. 95 p. c. alc. with more sep. of paraffin.

As will be seen from the above, the acid-, ester- and acetylation-values of the Miltitz oil are higher than those of the Bodenbach sample, the former being moreover the more soluble. These properties are obviously connected with the fact that the Miltitz raw material had been more thoroughly exhausted by distillation.

Rose Oil, Bulgarian. The fears which we expressed in our April *Report* have not only been confirmed by the actual result of the present year's crop, but the pessimistic rumours were far exceeded by the actuality. Now that the statistical returns are available it is shown that the total production of rose flowers amounted to 11 365 000 kilos, and as the oil-field all through the season was a very poor one, about 3800 kilos flowers being required to produce 1 kilo of oil, the entire result of the distilling amounted to 2987 kilos of rose oil. This quantity was distributed over the various districts as follows:—

District of Kazanlik	1070 kilos
" " Stara-Zagora	184 "
" " Nova-Zagora	145 "
" " Tchirpan	137 "
" " Karlovo	1004 "
" " Brezovo	363 "
" " Peschtira	58 "
" " Panagurichté	26 "

Total 2987 kilos

compared with " 3950 " in the year 1911¹⁾.

¹⁾ According to our informant, in the official statistics for the year 1911 (see October *Report* 1911, pp. 76 and 77) over 30 villages are missing, and the actual output for that year was 3950 kilos.

The report of the Bulgarian Ministry of Agriculture gives the flower crop as 9 525 000 kilos and the oil-production as only 2710 kilos, but our informant assures us that his own statements are the more accurate. For the flowers 60 centimes per kilo was paid this year, the highest price on record. The considerable increase in the quotations of rose oil which was necessary to make last May is sufficiently justified by the statements made above. The tendency continues firm and we scarcely think that anything is to be gained by putting off the time of buying still further.

In view of the inordinately high prices of the natural oil we recommend to the attention of our customers our substitution-products Rose Schimmel & Co. (Red Rose) and Synthetic Rose Oil Schimmel & Co., both of which are described on p. 124 of the present *Report*.

Rose Oil, German. In contradistinction to the failure of the crop in Bulgaria our plantations at Miltitz which, as already stated, have been considerably enlarged last year, have this season given an unusually abundant yield, all the conditions for the favourable development of the flowers having been fulfilled by the state of the weather in May and June. The reason why, in spite of this fact, we have distilled but little rose oil is that the manufacture of our speciality Rose Schimmel & Co. "Red Rose" (see p. 124) has absorbed very large quantities of flowers. Rose water is again available in sufficient quantities.

As was to be foreseen, the scarcity of rose oil has been responsible for the display of considerable energy on the part of sophisticators.

We give below a comparison of several samples of rose oil which have lately been submitted to us for our opinion or offered to us for sale, all of which, as a result of examination, had to be rejected as adulterated. For purposes of comparison we also quote the limits of value which have been observed by us in commercial oils of normal condition.

The samples Nos. 1 to 3, besides showing too high a refractive index, possessed too great a total geraniol content, which points to the presence of palmarosa oil or of a similar substance. In addition, No. 1 contained about 3 p. c. spirit.

In Nos. 4, 5 and 8, and particularly in No. 9, the high optical rotation caused suspicion of an addition of gurjun balsam oil, to the employment of which for the purpose of adulterating rose oil attention was called in our last April *Report*, p. 108. Samples Nos. 5 and 8 also contained spirit, an admixture which was likewise observed in Nos. 6 and 7.

A more thorough examination was in most cases impossible, partly because the quantity of oil submitted to us was insufficient even for the determination of the usual constants, as is shown by the hiatus in several parts of the table.

Rose oil	Original oil									Normal Commercial oil
	No. 1	2	3	4	5	6	7	8	9	
.....	0,8600	0,8604	0,8615	0,8635	0,8597	0,8620	0,8701	0,8652	0,8825	0,849 to 0,863
.....	- 0°37'	- 1°44'	- 2°27'	- 4°40'	- 4°20'	- 1°50'	- 1°3'	- 6°20'	- 10°17'	- 1° to - 4°
.....	1,46618	1,46529	1,46499	1,46300	1,46151	—	—	—	1,47210	1,452 to 1,464
pt.	+ 25°	+ 22,3°	+ 18°	+ 19,2°	+ 17,3°	—	—	—	+ 12,2°	+ 18° to + 23,5°
v.	1,4	0,6	1,4	—	1,2	—	—	—	—	up to 3
v.	10,7	9,3	18,7	—	14,8	—	—	—	—	7 to 16
Quantity of added alcohol (90 p.c.)	•									
ut	3 p.c.	—	—	—	5 p.c.	6 p.c.	9 p.c.	11 p.c.	—	—
Oil shaken out with water										
.....	0,8611	0,8605	0,8617	—	0,8619	0,8649	0,8749	0,8706	—	—
.....	1,46737	1,46757	1,46618	—	1,46698	—	—	—	—	1,466
geraniol ..	80,3 p.c.	79,5 p.c.	77,2 p.c.	—	71,7 p.c.	—	—	—	—	66 to 75 p.c.

From *Die Chemische Industrie*²⁾ we call the following particulars concerning Anatolian (Asia Minor) rose oil³⁾, an article which is occasionally heard of, but which, commercially speaking, plays a quite subordinate part.

In the year 1910 the rose oil industry which was established in the Vilayet of Konia about 15 years ago by Turkish emigrants from Bulgaria, has given excellent results. The year's output amounted to 60 000 miscals⁴⁾ (288,6 kilos), which brought a return of 7000 £T. (129 080 *M*) as compared with 45 000 miscals (216,45 kilos) representing a value of 5000 £T. (92 400 *M*) in the year 1909. As a rule from 8 to 14 okes (10,256 to 17,948 kilos) of roses are required to produce 1 miscal oil; and for this quantity of flowers from 40 to 52 paras (18,44 to 23,972 pfennigs) is paid. The price paid for the oil depends upon the solidifying point. Up to 10° it is 40 paras (18,44 pfennigs) per degree per miscal, between 10 and 15° it is 52 paras (23,972 pfennigs) per degree, with an advance of 40 paras, and for oils of a higher solidifying point it is 52 paras per degree, with an advance of 60 paras (27,66 pfennigs).

Konia rose oil is much esteemed by Constantinople traders for use as an admixture to an Indian aromatic essence which is known as "parfum impérial". The price of this essence, which is also brought into commerce as "genuine rose oil", is 250 Piastres (46,10 *M*) per oke.

¹⁾ The alcohol was isolated as such.

²⁾ *Chem. Industrie* 35 (1912), 178.

³⁾ *Comp. Report* April 1902, 60; April 1905, 68.

⁴⁾ 1 miscal = 4,81 grams; 1 oke = 1,282 kilo; 1 £T = 100 piasters = 18,44-*M*; 1 para = 0,461 pfennig.

According to the figures given, from 2132,2 to 3731,3 kilos of Anatolia roses are needed to produce 1 kilo of oil, that is to say on an average the same weight as in Bulgaria, while in Germany from 5000 to 6000 kilo flowers of the same species of roses are needed to produce 1 kilo of oil. But as the particulars quoted above are obviously inaccurate so far as the pecuniary returns are concerned (according to them the cost of a kilo of oil would amount to from 447,25 to 426,89 Marks), the other data must probably also be accepted with reserve, at any rate, we must leave to the writer of the article the responsibility for their accuracy.

Rosemary Oil. Business in the two varieties listed by us has been rather quiet and there is consequently but little to report. The French producers continue to complain of the keen competition offered by the Spanish distillers, whose oil has gradually reached such a degree of excellence that it cannot now be classed as inferior, either in respect of odour or of physical properties. From the producing centres in Tunisia we have received no news whatever lately. Dalmatian rosemary oil is obtainable in sufficient quantities. Owing to the alteration in the denaturing regulations in Germany the consumption of this variety of oil has fallen off considerably.

Rosewood Oil. In our *Report* of April 1911, p. 97, we discussed an article by E. Holmes on the botanical origin of *Lignum Rhodium*, in which *Genista canariensis* or *virgata* was mentioned as the probable parent-plant of this drug. Since that time, Holmes¹⁾ has been in correspondence with Dr. G. K. Perez, of Teneriffe, from whom he has obtained many interesting data concerning *Lignum Rhodium*. According to Perez, the Canary rosewoods were mainly *Convolvulus Scoparius*, commonly called "Retamon" or "Lena Noel" by the peasants. *Retamon*, however, is also the local name for *Genista canariensis*. It is not surprising that the two plants should be confused, for when not in flower they resemble each other so closely as to deceive even botanists. In Teneriffe, *Convolvulus floridus* is known as *Guiadil*. Its wood has a much fainter odour than that of *Convolvulus Scoparius*. The latter was formerly exported in such quantities (Dr. Perez believes to Germany), that the plant has been almost eradicated. *Genista virgata* is extremely rare in Teneriffe and has only recently been refound there by a German botanist. It appears to be only a variety of a *Genista* species which is very common in the island. Perez does not believe that the wood of *Genista virgata* is rose-scented, but of *Convolvulus Scoparius* he declares that the wood possesses such a powerful aroma of roses that a small piece of it is sufficient to scent a drawer with clothes. *Convolvulus Scoparius* has a variety *virgatus* Choisy, which may possibly have led to the belief that *Genista virgata* is the parent-plant of *Lignum Rhodium*.

¹⁾ *Perfum. and Essent. Oil Record* 3 (1912), 224.

Rue Oil. The great drought in Spain and Algeria has much impeded the distillation of sufficient quantities of oil, and has, in fact, made distilling impossible in certain districts. It has therefore been necessary to pay high prices for the few small lots of good quality which were to be found. We have had to alter our selling-prices in accordance with this fact.

Sage Oil. The distillers in Istria and Dalmatia supply sufficient oil to meet the requirements at unaltered cheap rates, and the position of the article affords no cause for comment.

Sandalwood Oil, East Indian. Careful readers of our *Reports* will not be surprised to hear that the prices of sandalwood oil have made a further advance in the course of the summer. It will be remembered that for more than a year we have clearly foretold the present upward movement.

The stocks of cheap wood are completely exhausted, and as the calculations of value of the oil now require to be based upon the prices paid for wood at the last auctions it is a matter of course that the quotations of oil must be increased. As for a considerable time past we have advised our customers to avail themselves of the cheap rates while there was time, no one will find fault with us for now asking an advance. A further rise in the market is probable in the future, for the Mysore Government will certainly take care that the wood which is to be offered for sale at this year's auctions is not disposed of at lower prices than those paid at the previous sales. We have again advanced our quotations in our October list and there is no doubt that we shall have to ask for further increases in case of large contracts to be delivered next year.

The annual auction sales of sandalwood of the Mysore State will be held at the undermentioned koties on the date specified against each, by the District Forest Officer in conjunction with the Deputy Commissioner of the District or an Assistant Commissioner deputed by the Deputy Commissioner:—

Serial No.	District	Koti	Date of sale	Approximate quantity in tons	Remarks
1	Mysore	Hunsur	18 th Nov. 1912	500	
2	id.	Seringapatam	21 st " "	275	
3	Bangalore	Bangalore	25 th " "	125	Includes about 30 tons of Tumkur and 5 tons Kolar district wood
4	Hassan	Hassan	28 th " "	150	
5	Kadur	Chickmagalore	2 nd Dec. "	300	
6	id.	Tarikere	5 th " "	275	Includes about 5 tons of Chital drug district wood
7	Shimoga	Shimoga	9 th " "	500	
8	id.	Sagar	12 th " "	100	
9	id.	Tirthahalli	16 th " "	225	
				total tons 2450	

Details as to assortments and lots of sandalwood to be exposed for sale as above in each kotie, together with the terms of sale, will be published as usual about the end of October 1912.

We set forth below the analytical values of four samples of sandalwood oil which have been submitted for our opinion. Of these, No. 1 does actually correspond to an East Indian Oil, but, as further investigation showed, it was abnormal to this extent that it contained terpin hydrate. As up to the present this body has not been observed as a normal constituent of East Indian sandalwood oil, and could not be found in a distillate of our own which was examined for purposes of comparison, it must have been added to the sample in question. If the oil has not been deliberately adulterated, the terpin hydrate may have got into it by some mistake.

Sample No. 2, which was emptied out from sandalwood oil capsules, was suspect on account of its insolubility in 70 p. c. alcohol, its excessive ester value and its exceptionally high santalol content. After being distilled by steam the sample, in addition to a normal solubility and increased optical rotation, showed a diminished ester value and a reduced santalol content, and then agreed with a normal sandalwood oil. The distillation-residue (7,8 p. c.) was liquid, soluble in alcohol, insoluble in light petroleum, and gave sap. v. 173,4, from which characters it was identified as castor oil.

Sample No. 3 was shown to be a highly-adulterated product by its altogether abnormal constants, and by its santalol content, which was only 51,3 p. c.

In the last oil-sample of our table, of which only a few grams had been sent to us, we were able to detect the presence of about 30 p. c. of spirit, while furthermore the optical rotation of the oil when freed from alcohol was found to be much too low, and thus pointed to an additional form of adulteration.

Sandalwood oil	No. 1	2		3	4	
		Original oil	Distilled with steam		Original oil	Freed from alcohol
d_{150}	0,9749	0,9759	—	0,9355	0,9207	—
α_D	—17° 18'	—16° 50'	—18° 1'	—14° 19'	—6° 45'	—10° 10'
Sol. in 70 p. c. alcohol	5 vols. & m.	10 vols. & m.	4,7 vols. & m.	1 v. 90 p. c. alc. & m.	—	—
Acid v.	2,8	3,5	1,8	2,8	—	—
Ester v.	10,4	24,6	11,3	9,1	—	—
Ester santalol	4,1 p. c.	9,7 p. c.	4,4 p. c.	3,6 p. c.	—	—
Total santalol	92,1 p. c.	98,2 p. c.	94,8 p. c.	51,3 p. c.	—	—
Distillation-residue	—	—	7,8 p. c.	—	—	—
Sap. v. of latter	—	—	173,4	—	—	—
Spirit	—	—	—	—	30 p. c.	—

It was well-known already that the wood of sandal trees growing on dry, rocky, mountainous soil is harder and richer in oil than that of trees cultivated in fertile soil¹⁾, and this belief is confirmed by investigations made by Puran Singh²⁾. The wood examined by him was grown on soil of the most widely varying character. For the purpose of determining the oil-content, Singh adopted three different methods: 1. The wood-dust obtained by means of a rasp-file was subjected to steam-distillation. 2. The wood-dust was extracted with ether in a Soxhlet apparatus. 3. The wood-dust was boiled in alcohol in a reflux-condenser or macerated in cold alcohol during one week. By mixing the oils obtained from the different samples of wood, Singh prepared an average sample which possessed the following constants: d_{20}^0 0,9765, α_D — 15,6 to — 16°, sap. v. 9,72, ester v. after acet. 211,3, santalol-content, calc. according to the formula $C_{15}H_{26}O = 99,4$ p. c. Converted into the true formula for santalol, $C_{15}H_{24}O$, the santalol-content of the sample would amount to 98,65 p. c. These values do not agree with those observed for normal oils, which is probably accounted for by the fact that, as the author himself indicates, the wood was not sufficiently exhaustively distilled. For this reason it is unnecessary to enter into further consideration of the values given by Singh.

M. Rama Rao³⁾ reports on the plants which serve as hosts of the sandal tree; that tree, as was shown a long time ago, being a root-parasite⁴⁾. Rama Rao enumerates no fewer than 144 species upon whose roots the haustoria of the sandal tree have been detected. He has furthermore prepared a list of 252 plants with which the sandal tree is found in association.

Sandalwood Oil, West Indian. No changes in prices are to be reported. We have continued to import by far the greater part of the supplies of West Indian sandalwood. Our excellent distilling plant enables us to offer the article at advantageous prices and for large contracts we are prepared to submit special offers.

On the detection of β -caryophyllene in West Indian sandalwood oil, see p. 149.

Sassafras Oil. Our New York branch reports that some difficulty has occasionally arisen in procuring sassafras oil of reliable quality and that as a result of this the tone of the market is firm. The information supplied by our friends relates of course to the position in the producing districts, for in New York there is never any scarcity in the article, because

¹⁾ Gildemeister and Hoffmann, *The Volatile Oils*, 1st Ed., p. 339.

²⁾ *Forest Bulletin* No. 6, 1911, Calcutta.

³⁾ *Indian Forest Records* 2 (1911), Pt. 4. Quoted from *Bull. Imp. Inst.* 10 (1912), 325.

⁴⁾ *Comp. Report* October 1904, 84; April 1905, 74.

sassafras oil has always been subject to adulteration with certain fractions of camphor oil, safrol, &c. which it is very difficult to detect.

Savin Oil. J. W. Agnew and R. Croad¹⁾ in a paper read before the Society of Public Analysts and other Analytical Chemists, report that in the fractions of a saponified savin oil passing over at up to 160° they have detected the presence of α -pinene. They identified the body by oxidising with mercuric acetate into sobrerol (m. p. 131°) and 8-hydroxy-carvotanacetone (m. p. of the semicarbazone 175°). From the sobrerol they obtained the dibromide (m. p. 131 to 132°) and the pinol-dibromide (m. p. 94°)²⁾. The pinene fraction amounted to 1,7 p. c. of the original oil. We ourselves had been unable to identify pinene in savin oil³⁾, although we have found the oil to contain a small fraction with the b. p. of pinene. It would therefore appear as if the method employed by Agnew and Croad is better adapted for the detection of small quantities of pinene than is the preparation of the nitrosochloride which we had attempted at the time. The other constituents were: about 16 p. c. *l*-sabinene, 5,3 p. c. terpinene (m. p. of the nitrosite 155 to 157°)⁴⁾ and 17 p. c. sabinol (b. p. 208 to 209°; $d_{15} 0,9391$; $[\alpha]_{D15} + 17,04^\circ$). The constants of the sabinene were as follow: b. p. 162 to 166°, $d_{20} 0,8468$, $[\alpha]_{D15} - 42,5^\circ$. When the sabinene fraction was treated with mercuric acetate oxidation immediately ensued, and after 15 minutes a large quantity of mercurous acetate had been formed. With pinene, on the other hand, oxidation only sets in after the lapse of one hour.

The saponification-liquor of savin oil contained, in addition to formic and acetic acid, a saturated acid, m. p. 85°.

It is remarkable that the oil, which is said to have been supplied by us, should have been lævorotatory, whereas all savin oil which we have observed up to the present has been dextrorotatory. H. E. Burgess also (as he stated in the discussion on Agnew and Croad's paper), has hitherto only observed dextrorotatory savin oils.

Among the numerous savin oils investigated by the authors, only the lævorotatory product contained the normal quantity of sabinene, whereas all the other samples only contained small proportions of this hydrocarbon, but considerable proportions of pinene. From this fact Agnew and Croad draw the conclusion that the last-named oils had been sophisticated with turpentine oil. In our opinion it is also possible that the raw material of the samples which were rich in pinene was partly derived from *Juniperus phœnicea*, L., of which the oil contains a fairly large proportion of pinene⁵⁾.

¹⁾ *Analyst* 37 (1912), 295.

²⁾ *Comp. Report* October 1909, 167.

³⁾ *Report* April 1908, 84.

⁴⁾ *Report* April 1911, 106.

⁵⁾ *Comp. Report* April 1906, 61.

For chemical proof in legal investigations of poisoning by savin oil, J. Hämäläinen¹⁾ avails himself of the property of sabinol to combine in part, within the human organism, with glucuronic acid, and to appear in the urine in the form of sabinol-glucuronic acid. This acid yields a well-defined strychnine-salt which crystallises with two molecules of water and melts at 196 to 197°; $\alpha_{D20} - 39,66^\circ$. It is sparingly-soluble in cold water, but dissolves fairly readily in hot water. At room-temperature it is sparingly-soluble in alcohol, ether, acetone, acetic ester, benzene, chloroform, and light petroleum.

Shiu Oil. We have already on several occasions called attention in these *Reports*²⁾ to the statement that Formosa produces a species of tree allied to the camphor tree, which yields an oil rich in linalool. The oil yielded by the tree has already been thoroughly examined years ago by Keimazu³⁾ under the name of Apopin oil or Shú-yu, while recently K. Nagai has published an illustrated pamphlet on the subject in the Japanese language, in which the oil is referred to as Shiu Oil. Samples of the oil, or of fractions of the oil, have also made their appearance from time to time, but there has been no news of any subsequent deliveries of the article. A similar sample is now again described in a British periodical⁴⁾ under the name of Shiu Oil. As a matter of curiosity we here reproduce briefly the properties of this sample as quoted in the paper in question: The oil possessed a very agreeable odour, reminding of Cayenne linaloe oil; $d_{20} 0,870$; $\alpha_D - 14^\circ$; $n_{D20} 1,4606$; sap. v. 0; total linalool estimated by acetylation 62,3 p. c.; soluble in 2 vols. 70 p. c. alcohol.

According to these data the constants of the oil resemble those of Cayenne linaloe oil, but it differs from that oil in its linalool-content, which is materially lower. But this may be connected with the method in which the acetylation has been carried out; for in the case of linalool this must not be conducted in the ordinary way, as in that case the results will be far below the actuality⁵⁾.

Spearmint Oil. The representative sent out by our New York branch has again paid repeated visits to the producing districts in Michigan and Indiana this summer, and has ascertained the total area under cultivation to be 2057 acres. In 1911 there were only 1520 acres under spearmint, hence the production will be increased by the yield of 537 acres. An area of 1100 acres has been newly planted; the whole of it by one farmer.

¹⁾ *Biochem. Zeitschr.* 41 (1912), 241. Quoted from *Apotheker Ztg.* 27 (1912), 487.

²⁾ *Report* October 1910, 26, 79; April 1912, 92.

³⁾ *Report* October 1902, 10; April 1904, 10.

⁴⁾ *Perfum. and Essent. Oil Record* 3 (1912), 124.

⁵⁾ Compare with regard to this our *Report* of April 1907, 119. Gildemeister u. Hoffmann, *Die ätherischen Öle*, 2nd Edition, Vol. I, p. 597.

As the stocks of old oil are entirely exhausted and as the article is gaining popularity year by year in the confectionery-industry, while the production is moreover entirely controlled by a few large firms, it is believed that there is no probability of a reduction in prices, notwithstanding the increased area under cultivation. On the contrary, the market wears a very firm aspect.

Spike Oil. During the last few months a very brisk turnover in this article, which, as is well known, is used in large quantities and in multifarious industries, has depleted our stocks, and we are therefore anxiously awaiting the arrival of the new season's oil. In a few districts of Southern France the producers refuse point-blank to distil spike oil at all unless they can obtain at least 9 or 10 fcs. per kilo for it. Labour is scarce in the mountain districts, and can only be attracted by the payment of high wages. But only those firms who use spike oil merely for the purpose of "cheapening" lavender oil can afford to pay such prices for it, for in this lucrative trade a few francs more or less are of no importance. It is therefore probable that Spain will again be called upon this year to supply the bulk of the spike oil required. This country, in addition to numerous inferior qualities, produces an oil which is quite equal to the French in every respect, and as there are plenty of enquirers the producers are standing out for considerably higher prices. A few weeks must still elapse before the market settles down.

Star Anise Oil. The market position of this important article can be most readily surveyed by a glance at the table of prices below. The quotations there given are "cif" and refer to unimpeachable quality with a normal congealing point.

Quotations of star anise oil: —

on 1 st April	5/9	on 1 st July	5/5
„ 15 th „	5/7	„ 15 th „	5/6
„ 1 st May	5/4	„ 1 st Aug.	5/7
„ 15 th „	5/2	„ 15 th „	5/7 ¹ / ₂
„ 1 st June	5/4	„ 1 st Sept.	5/8
„ 15 th „	5/1	„ 15 th „	5/11 ¹ / ₂ .

It will be seen that the prices are once more tending upwards, and if the crops of Russian anise and of fennel should be unfavourable it is probable that there will be a further considerable increase in the quotations. The question of the production continues to be surrounded with mystery and it is therefore impossible to form any opinion on the future of the article from, say, statistical data. It does not appear that considerable stocks of cheap oil have been carried forward from 1911 either in Europe or in the United States.

In our last *Report*¹⁾ we stated that A. W. Mann, of London, as well as ourselves had met with sparingly-soluble star-anise oils. Mann, in the case of the oils examined by him, suspected adulteration with cedarwood oil, whereas in our samples we were able to detect the presence of fatty oil. Parry²⁾ appears to have examined oils of a similar character, for he mentions two samples of which the sp. gr., the co-efficient of refraction and the congealing point were too low and the solubility insufficient. Another sample which deviated still more from the normal (the cong. pt., for instance, being only 7°). was found upon closer examination to be adulterated with about 40 p. c. of mineral oil.

Tansy Oil. This article has undergone several advances in price during the last few months, because the output has been less than in 1911, and because this reduction in the supply was accompanied by an exceptionally brisk demand. According to information collected by our New York branch the total area under tansy in the State of Michigan is 131 acres, while in 1911 it was 145 and in 1910 as much as 182 acres. And whereas at the time of distilling in 1911 there was still on hand a stock of nearly 1300 lbs. of the previous year's oil, the balance now available from last year only amounts to about 300 lbs. In the circumstances there is every reason for describing the position of tansy oil as very firm.

Oil of *Taxodium distichum*. As we stated in our October Report of 1911, p. 87, A. F. Odell³⁾ has discovered in the oil from the wood of Southern Cypress (*Taxodium distichum*, Rich.), a North American conifer, an aldehyde to which at the time he gave the name of cypral. With the object of obtaining a larger quantity of this aldehyde, Odell⁴⁾ has recently prepared the oil from the cones of the tree in question, but without result, the oil proving to be free from aldehyde. The cones, distilled in September, yielded 1 p.c. yellowish green oil with an odour of pinene; the cones which had been collected later in the year yielded 1,5 to 2 p. c. oil of a darker colour and an odour more resembling that of lemons. d_{40}^0 0,86 and 0,850; $\alpha_D + 18,0$ and $+ 35,5^\circ$, alcohol-content 2,5 p. c. The oil contained about 85 p.c. d- α -pinene (b. p. 156 to 157°; d_{40}^{180} 0,8616; $[\alpha_D] + 30,8^\circ$; $n_{D20} 1,4655$) and 5 p.c. d-limonene (b. p. 175 to 180°; d_{40}^{180} 0,8567; $[\alpha]_{D20} + 98,3^\circ$; $n_{D20} 1,4742$; m. p. of the tetrabromide 104°, of the nitrosochloride 105°), as well as 2 p. c. of a dextrorotatory fraction which probably contains a *pseudo* terpene alcohol, as was apparent from the formation of a copious, brown, flocculent mass upon the addition of Beckmann's mixture. The distillate also

¹⁾ *Report* April 1912, 120. Owing to a printers' error we refer here (line 12 from the top of the page), to "readily-soluble" star-anise oils; this should of course be "sparingly-soluble".

²⁾ *Chemist and Druggist* 81 (1912), 372.

³⁾ *Journ. Americ. Chem. Soc.* 33 (1911), 755.

⁴⁾ *Ibidem* 34 (1912), 824.

contained 3 p. c. carvone (d_{40}^{180} 0,960; n_{D20} 1,500; m.p. of the semicarbazone 162 to 163°), as well as 3 p. c. of a dextrorotatory tricyclic sesquiterpene probably identical with the sesquiterpene from the wood oil. This sesquiterpene gave: d_{40}^{180} 0,9335, n_{D20} 1,5039.

Thyme Oil. All varieties continue to be in stock in sufficient quantities, and there are no fluctuations in price to report. In spite of the great drought, the producing centres again appear to be sending satisfactory supplies to market this year.

Oil of *Thymus hyemalis*. Up to the present nothing definite was known as to the parent-plant of the so-called Spanish "verbena" oil. Only recently J. C. Umney¹⁾ has been furnished from Spain with a supply of authentic distilling-material, which has been identified by E. M. Holmes as *Thymus hyemalis*, Lange. This species is nearly related to *T. hirtus*, Willd. and *T. vulgaris*, L. Boissier placed it under *T. Mastichina*, L. and Pourret under *T. sparsifolius* var. *hyemalis*. Its habit of growth varies considerably, but it is easily distinguishable from the other *Thymus*-species. Umney's article contains illustrations of the entire plant as well as of the bracts and parts of the flower.

Turpentine Oil. C. H. Herty²⁾, in a profusely illustrated pamphlet, describes a new method of tapping for the purpose of preparing turpentine. It is known as the "light chipping" method and its principal advantage is that the tree is wounded less deeply than by the old boxing method. As a result of experiments made at Walkill, and extending over 4 years, Herty finds that with the "light chipping" method it is possible to tap the trees for an indefinite time, while the turpentine yield is larger than by the older method. Moreover, the loss of economically valuable wood is much smaller than with the older treatment.

Recent reports concerning the turpentine oil industry in British India have been very favourable. According to a communication by the Forest Administration of the United Provinces³⁾, the profit derived from the exploitation in the district of Naini-Tal in the past year was 85195 Rupees, as compared with 38705 Rupees in the previous year. Extensive preparations have been made for increasing the turpentine output. The trees are only tapped once every 15 years, 250000 trees being tapped each year.

An illustration of a "Chir" tree (*Pinus longifolia*) in course of tapping is given on p. 139 of R. S. Pearson's book "Commercial guide to the forest economic products of India", which we review in p. 130 of the present Report.

¹⁾ *Perfum. and Essent. Oil Record* 3 (1912), 212.

²⁾ *Relation of light chipping to the commercial yield of naval stores*. U. S. Department of Agriculture, Forest Service. Bull. 90, 1911.

³⁾ *The Indian Trade Journal* 25 (1912), No. 314, p. 25.

The Russian Pharmaceutical Journal (1912, Nos. 1 to 6)¹⁾ contains a series of articles in the Russian language by J. K. Maisit on "Investigations into the heart-sap of the Pine, Spruce and Fir in Russia, and in Turpentine oil from White Pine Resin (*Pinus silvestris*, L.)". The author was good enough to inform us that these articles would shortly also be published in German. From an extract which he sent us at the same time we take the following: The common pine has been utilised for resin in Russia since the year 1780; colophony and turpentine oil being likewise produced, although not in large quantities. This turpentine oil is known in Russia by a term which, literally translated, signifies "sulphur turpentine oil".

The first part of Maisit's work describes the experiments in the economic production of resin which have been carried out in Russia by various investigators, including the author himself. The second part is chiefly devoted to Russian turpentine oil. This oil is as yet little known, to which must be added the fact that pine tar oils are also brought into trade in Russia under the name of turpentine oil.

Maisit states that Russian turpentine oil contains the following constituents: *d*-pinene, small quantities of acetone, dipentene, *l*-limonene, *i*-sylvestrene (m. p. of the inactive hydrochloride 72 to 73°), and *d*-terpineol.

Our *Report* of October 1910 contained on p. 140 an abstract of a paper by C. T. Kingzett and R. C. Woodcock on the formation of formic- and acetic acids by the atmospheric oxidation of turpentine oil. The authors have continued their investigations²⁾ and have observed that, when turpentine oil is exposed to atmospheric oxidation hydrogen peroxide is formed in addition to formic- and acetic acids. It is as yet impossible to explain for certain how these compounds are generated from turpentine oil, but it is not impossible that they may be due to the action of water upon one or more organic peroxides. Neither is it improbable that formic and acetic acids may first be formed secondarily from primarily-produced formaldehyde and acetaldehyde.

Space does not permit us to refer in detail to the authors' numerous experiments. We can only note that mixtures of water and American or Russian turpentine oil, as well as of the hydrocarbons pinene and sylvestrene, prepared from these oils by repeated distillation, were oxidised as far as possible by passing air through them. The resultant quantities of formic and acetic acid as well as of hydrogen peroxide were determined quantitatively.

In the preparation of pinene from turpentine oil, first and last runnings remain behind which, mixed together, are brought into trade and are added

¹⁾ *Chem. Zentralbl.* 1912, I. 1832.

²⁾ *Journ. Soc. Chem. Industry* 31 (1912), 265.

to turpentine oil. According to H. Wolff¹⁾ such additions are scarcely capable of detection. On the one hand, when it is being distilled with turpentine oil, the greater part of the last runnings passes over at a lower temperature than when fractionated by itself; on the other, when the mixture is treated with concentrated or fuming sulphuric acid much more material is separated out from it than was to be expected from the quantity of the residue. It would appear that in the presence of high boiling turpentine oil constituents the action of the sulphuric acid loses in intensity. In the case of pure turpentine oils also, as soon as resinification has perceptibly advanced, treatment with sulphuric acid results in increased separation. When the evaporation-residue has but slightly increased, and the separation with fuming sulphuric acid shows a marked increase, the addition of waste-products to the turpentine oil under examination may be suspected. Where the resinification is considerable, there is no means of distinguishing at all.

With the object of testing turpentine oil for the presence of petroleum distillates or colophony, R. Marcille²⁾ ascertains the quantity of 90 p. c. acetic acid which is required to dissolve a given quantity of turpentine oil. As the degree of solubility of turpentine oil and its adulterants differs, the presence of additions may thus be ascertained. Another method adopted by Marcille is to mix turpentine oil with sulphuric acid in an apparatus devised by Tortelli, and to determine the increase of temperature which results as an indication of the presence of adulterants.

Some time ago we referred to the apparatus for the estimation of benzines in oil of turpentine by means of fuming nitric acid which has been described by Marcusson and Winterfeld³⁾. Marcusson⁴⁾ has now proposed a modification of the method, by which 10 cc. of the oil under examination is introduced in the course of about half an hour into 30 cc. fuming nitric acid (d 1,52), the acid having been previously brought to a temperature of -10° in the glass apparatus devised by Marcusson and Winterfeld. After about 15 min. from 75 to 80 cc. cooled concentrated (not fuming) nitric acid (d 1,4) is added. If no oily separation now becomes perceptible upon the acid, the oil is free from benzine. The paper further describes methods for testing for benzene hydrocarbons and for the simultaneous estimation of benzine and benzene hydrocarbons, for the particulars of which we refer to the original.

As the outcome of his investigations, Marcusson has found that the nitric acid method is suitable for the estimation of benzine and of benzene

¹⁾ *Farbenztg.* **17** (1912), 1492. Quoted from *Chem. Zentralbl.* **1912**, I. 1930.

²⁾ *Bull. Soc. chim.* IV. **11** (1912), 762.

³⁾ *Chem. Ztg.* **33** (1909), 987; *Report April 1910*, 114.

⁴⁾ *Chem. Ztg.* **36** (1912), 413, 421.

hydrocarbons, and for the simultaneous detection of benzine and benzene compounds in turpentine oil mixtures. In this connection it must be borne in mind that the results are independent of the character of the benzine, that is to say the method applies equally to Russian or Pennsylvanian benzines, which are poor in natural benzene hydrocarbons, and to Indian or Galician benzines, which contain large proportions of these bodies.

H. Wolff¹⁾ regards Herzfeld's method for the estimation of benzene in turpentine oil²⁾ as unreliable. He thinks that it may only be of value for qualitative detection and even in that case only when the test has a positive result and when it agrees with the other constants. For the exact estimation of benzine and benzene hydrocarbons Wolff prefers Marcusson's method³⁾.

For the purpose of detecting the presence of wood-turpentine in American oil of turpentine, E. J. Parry⁴⁾ proposes the estimation of the bromine-, or better still of the iodine-value. The iodine-value of wood-turpentine is 230 to 300, the iodine-value of the last 10 p. c. of the distillation being lower still. For American turpentine oil the iodine-value is 360 to 375 (Hübl) or 335 to 350 (Wijs) and for the last 10 p. c. according to both methods not less than 350.

For testing American turpentine oil for petroleum hydrocarbons, Parry recommends Eibner and Hue's⁵⁾ sulphuric acid method.

The test for pine tar oil recommended by Piest⁶⁾ (black decoloration upon treatment with acetic anhydride and hydrochloric acid) has been submitted to a control-test by H. Wolff⁷⁾, who has found that it is effective only with pine tar oils which in any case turn black or brown when treated with concentrated hydrochloric acid. The difference in solubility in acetic anhydride between pine tar and turpentine oils is fairly considerable. This test cannot be used for quantitative estimation, but it offers a means of estimating in a simple manner the minimum percentage of an addition of pine tar oil.

Wolff also reports on the waste-oils of sulphite cellulose manufacture which have been freed as far as possible from methyl mercaptane and methyl sulphide. Generally speaking these oils are less closely allied to turpentine oil than to the pine tar oils, which they greatly resemble in

¹⁾ *Farbenztg.* 17 (1912), 1553. Quoted from *Chem. Zentralbl.* 1912, I, 1931.

²⁾ *Comp. Report* April 1910, 111.

³⁾ *Comp. Report* April 1910, 109.

⁴⁾ *Chemist and Druggist* 81 (1912), 340.

⁵⁾ *Comp. Report* October 1910, 136.

⁶⁾ *Comp. Report* April 1912, 130.

⁷⁾ *Farbenztg.* 17 (1912), 1709. Quoted from *Chem. Zentralbl.* 1912, I, 762.

their chemical and physical properties. They differ among each other according to method of production, purification, and raw material. With respect to solubility the cellulose oils partly behave similar to turpentine and pine tar oils. For the purpose of distinguishing between cellulose oil on the one hand and turpentine and pine tar oils on the other, Wolff recommends certain colour reactions, into the details of which we cannot enter here.

H. Wolff¹⁾ has also established the toxic action of turpentine oil by experiments on mice. Injections of 0,12 to 0,17 g. turpentine oil in olive oil per 10 g. weight of the experimental animal were fatal; when the dose was gradually raised some of the animals began to accustom themselves to the oil to a considerable extent. The action of turpentine oil would appear to depend largely upon the quantity of oxygen which is absorbed; when oils are rich in oxygen a dose of 0,08 to 0,1 g. per 10 g. weight of the experimental animal is generally fatal. Pine tar oils behave similar to turpentine oils, the limits lay between 0,06 and 0,12 g.

T. W. Pritchard²⁾ has read a paper before the New York Section of the Society of chemical Industry on a new method of preparing wood turpentine³⁾. In order to attain a high output it is necessary that the temperature within the retort in which the wood is being distilled should be uniform. To ensure this, the retorts are furnished with double jackets between which oil is pumped in. Outside the retort is a heating-apparatus by means of which the oil can be brought to a given temperature. Before the beginning of the distillation hot steam is blown into the retort to expel the cold air from it. After this the oil is circulated into the space between the inner and outer shells of the jacket; a suitable oil for heating purposes being a certain petroleum residue which is difficult to decompose, and which (air being excluded) can be heated safely to from 315 to 370°. So long as any readily-volatile oils are passing over the temperature within the retort must not exceed 230°, but when all these products have passed over, it may be raised by degrees. One of the great advantages of this process is the comparative freedom from fire-risk, with the consequence of low insurance rates, these being a very considerable factor in other wood-distilling processes. The wood turpentine which is obtained by Pritchard's method is of excellent quality, but it still differs materially from gum turpentine oil by the presence in it of a small proportion of constituents resembling pine-tar oil. Pritchard, however, believes that he has discovered a method by which it will be possible to remove these constituents completely.

¹⁾ *Farbenztg.* **17** (1912), 1495. Quoted from *Chem. Zentralbl.* **1912.** I. 1919.

²⁾ *Journ. Soc. chem. Industry* **31** (1912), 418.

³⁾ *Comp. Report* April **1912**, 126.

From one cord of "Western wood", Pritchard obtained 40 gallons of a water-white turpentine oil, 1,5 gallons of a turpentine oil of second quality, 10,5 gallons light oil, 3,1 gallons light product (from heavy oil), 2,7 gallons light product (from extra heavy oil), 87,5 gallons heavy oil, 40,6 gallons extra heavy oil, 950 lbs. charcoal, and 138 lbs. residue.

Oil from the turpentine of *Abies cephalonica*, Link. This tree, which occurs on Mount Ainos in the Greek Island of Cephalonia, yields a resin which is locally used as a popular remedy, being used both internally, as an aperient, as well as externally in affections of the skin. J. Emmanuel¹⁾ has subjected this turpentine to closer examination. He describes it as a greyish-yellow mass of the consistency of honey, with an agreeable turpentine-like odour and a bitter and aromatic taste. Emmanuel has obtained from the raw material, among other bodies, 17,4 p. c. of a colourless essential oil which, at ordinary pressure, boiled between 89 and 175° and, at 15°, had sp. gr. 0,9279. Its rotation was -68° in a 200 mm. tube²⁾, $n_{D13,5^\circ}$ 1,4745. Emmanuel says nothing with regard to the constitution of the oil.

K. Dieterich³⁾ has been offered by exporters, through a Hamburg firm, a resin described by the sellers as *Gummi Thus*, which when carefully tested, proved to be an American fir-resin. The product does not contain gum, and is therefore no gum-resin, as might be assumed from the name. It yielded from 9 to 10 p. c. oil of which the constants agreed with turpentine oil (b. p. about 155°; $d_{18,5^\circ}$ 0,8667; $\alpha_{D20^\circ} + 13,35^\circ$; n_D 1,47644).

Larch turpentine oil. Our efforts, extending over several years, to procure authentic raw material for the distillation of larch turpentine oil have at last been crowned with success by the receipt, from an entirely reliable source, of a sufficient quantity of larch turpentine. This turpentine, after being filtered, was clear, of a faint yellow colour, and of a consistency just above the verge of liquescence. Its constants were as follow: $\alpha_D + 29^\circ 20'$; acid v. 69,5; ester v. 55,9; giving a clear solution with 3 parts of 80 p. c. alcohol, wholly soluble in light petroleum except for a few flakes. We obtained from it by steam distillation 13,5 p. c. of an oil possessing the following characters: d_{15° 0,8649, $\alpha_D - 8^\circ 15'$, n_{D20° 1,46924, acid v. 0, ester v. 5,9, soluble in 6 volumes and more of 90 p. c. alcohol. Behaviour on boiling in a Ladenburg flask (753 mm.) 157 to 161° 60 p. c., 161 to 164° 20 p. c., 164 to 168° 6 p. c., residue 14 p. c.

¹⁾ *Arch. der. Pharm.* 250 (1912), 104.

²⁾ Emmanuel's statement is not quite clear. He writes: „The polarisation was -68° in a 200 cm.-Tube Rh. according to Wild“. We assume that our reading of this statement is correct.

³⁾ *Pharm. Zentralkh.* 53 (1912), 652.

We availed ourselves of this opportunity to check, with this authentic material, a method proposed by L. E. Walbum¹⁾ for the testing of larch turpentine.

Walbum's method is as follows:

10 grams Venetian turpentine are dissolved in 30 grams ether, and placed in a closed flask on a small water-bath at a constant temperature of 20,5° C. After 10 minutes 8 cc. double-normal ammoniacal liquid, which has previously been brought to the same temperature, are admixed. The resulting completely clear liquid must congeal to the consistency of a jelly after being left standing for not more than 11 minutes.

The test with our larch turpentine showed that such a mixture does not congeal into a jelly within less than about 24 hours, and then only partially. As we have hitherto not heard of control-tests of Walbum's method, and as the material at our disposal was indisputably pure, we advise against the making of any claims based upon the method of examination referred to above, at any rate until further control tests have been carried out.

Oil of Umbellularia californica. Concerning the narcotic and antiseptic effect of umbellulon, see page 137.

Valerian Oil. No change is to be recorded in this article. The demand was slight, although we have a large number of regular customers for our own distillate, which is much preferred by them on account of the purity of its odour and its aroma.

Japanese valerian oil is offering cheaply in fairly large quantities, but it is generally difficult to find a market for it.

Vetiver Oil. We have experienced no lack of raw material of excellent quality for the preparation of our own distillate and we have therefore been able to replenish the gaps in our stocks which had been caused by the animated business of the spring season. Réunion vetiver oil has been exceedingly scarce. This article appears to have become the subject of speculative enterprise, for the prices have been rushed up to nearly double the old figure. It would seem at the same time that there has been no decrease in the production, for the shipments from St. Denis up to the end of July amounted to 443 kilos against 445 kilos in the corresponding period of 1911.

The Imperial Institute²⁾ in London reports on vetiver oils of different origin. An oil distilled in the Fiji Islands was of a dark green colour and showed the following constants: d_{15}^4 1,0298, sap. v. 35,3, sol. in 80 p. c.

¹⁾ Pharm. Zentralh. 49 (1908), 911.

²⁾ Bull. Imp. Inst. 10 (1912), 31.

alcohol, at first clear, but from 2,5 vols. upwards cloudy. Roots from the Seychelles afforded a total yield of 0,482 p. c. oil, of which 0,072 p. c. had been separated out from the distillation waters. The test of that part of the oil which had been obtained by direct distillation (0,41 p. c.), gave the following result: d_{150} 1,0282, $\alpha_{D200} + 27^\circ$, acid v. 55,9, ester v. 11,4, sap. v. 67,3; sol. in its own vol. 80 p. c. alcohol and more. The colour of the oil was a deep golden brown; the consistency was viscous. The oil recovered from the waters of distillation showed similar properties, but its odour was somewhat fainter than that of the principal oil.

Wallflower seed Oil. According to M. Matthes and W. Boltze¹⁾, the seed of wallflowers contains 0,0073 p. c. of a colourless essential oil, with an odour reminding of water-fennel. B. p. 120 to 125° (15 mm.); d_{150} 0,9034; $[\alpha]_D - 12,73^\circ$; n_{D200} 1,6920. The oil immediately discolours potassium permanganate and bromine. Combustion gave 85,68 p. c. carbon and 11,56 p. c. hydrogen.

We have already on a previous occasion²⁾ referred to the presence in wallflower seed of a sulphide: cheirolin.

Wintergreen Oil, American. No alteration can be reported in the position of this article. According to the reports from our branch-house there is no lack of pure oil, and the market shows a certain tendency towards easing off. We have already taken account of this weakness in our quotations. Oil from *Gaultheria procumbens* also, which, as is well-known, is only esteemed in the United States, is abundantly available.

Wormseed Oil, American. The high prices have had the result of considerably increasing the production within the last three years. Our New York branch has ascertained that the area under wormseed in 1910 amounted to about 90 acres and in 1911 to about 170 acres, while for the present year the area under cultivation may be put at 225 acres. The oil-output in 1910 was 2800 lbs. and in 1911, 5000 lbs., and it is therefore probable that it may reach 6700 lbs. this year. As there is also some stock of old oil left over in the hands of middlemen it is thought that lower prices may be anticipated. We do not believe that there will be a fall in prices worth mentioning, for owing to the well-established therapeutic efficacy of the oil the demand for it is steadily increasing.

Both E. K. Nelson³⁾ and O. Wallach⁴⁾ where engaged last year, almost simultaneously, in investigating the structure of ascaridol⁵⁾, which was discovered by us as a constituent of American wormseed oil. As appears

¹⁾ Arch. der Pharm. 250 (1912), 217.

²⁾ Comp. Report October 1910, 85.

³⁾ Comp. Report October 1911, 98.

⁴⁾ Liebigs Annalen 392 (1912), 59.

⁵⁾ Report April 1908, 109.

from Wallach's publication on the subject¹⁾, ascaridol, when suspended in water in the presence of colloidal palladium absorbs 4 atoms hydrogen with unexampled rapidity, in such a manner that it is necessary to regulate the supply of hydrogen in order to obviate the heat generated during the process becoming too powerful. The reaction gives rise to two bodies which are easily separated from each other. One is an oil which easily volatilises with steam; the other a less readily volatilisable, solid body. The latter is most readily isolated by extracting the residue with chloroform after the bulk of the volatilisable body has passed over. The solid reduction-product constitutes a new terpin: 1,4-terpin (terpinen terpin), and occurs in the form of bold prisms, m. p. 116 to 117°. This terpin may occur in two sterically isomeric modifications, of which that melting at 137° was described by Wallach²⁾ a few years ago. The body with m. p. 116 to 117°, therefore, would represent the second modification. The principal product which is formed when the 1,4-terpin is heated with oxalic acid is 1,4-cineol³⁾ (b. p. 172°; d_{180} 0,9010; n_{D180} 1,4479) which, when mixed with hydrobromic glacial acetic acid yields terpinene dihydrobromide (m. p. 58 to 59°). When subjected to persistent warming with potassium permanganate the result was not an acid corresponding with cineolic acid, but a sparingly-soluble acid, m. p. 157°, with a smaller oxygen-content. When 1,4-terpin is split up by oxalic acid it yields in addition to a large proportion of 1,4-cineol, a small proportion of an unsaturated alcohol. This alcohol cannot be obtained in the pure state but it was possible to identify its oxidation-product. For this purpose the decomposition-product of the terpin, distilled off with steam, was oxidised with 1 p. c. potassium permanganate solution at 0°, and the 1,4-cineol which was present blown off with steam. The residue contained a glycerol which, when heated with dilute sulphuric acid, was split up affording cymene and a ketone, Δ^1 -menthenone-3. Thus the presence of the original substance of Δ^3 -menthenol-1 was proved. Under continuous oxidation the two terpinenols of which the existence is possible, yield α, α' -dihydroxy- α -methyl- α' -isopropyladipic acid, which is easily identifiable by conversion into the dilactone. The author succeeded, in fact, by suitable treatment of the oxidation-liquors, in isolating a dilactone $C_{10}H_{14}O_4$ m. p. 72°. This affords the proof of the presence of a terpinenol in the reaction-product obtained from the terpin with oxalic acid and identifies the terpin itself as a compound of the terpinene series.

The oil which is formed in addition to terpin during the process of reducing ascaridol contains both saturated and unsaturated constituents. For this reason the body was further reduced in the presence of palladium and the ultimate residue of unsaturated substance removed with potassium

¹⁾ Nelson's paper appeared when the substance of Wallach's experimental work was concluded.

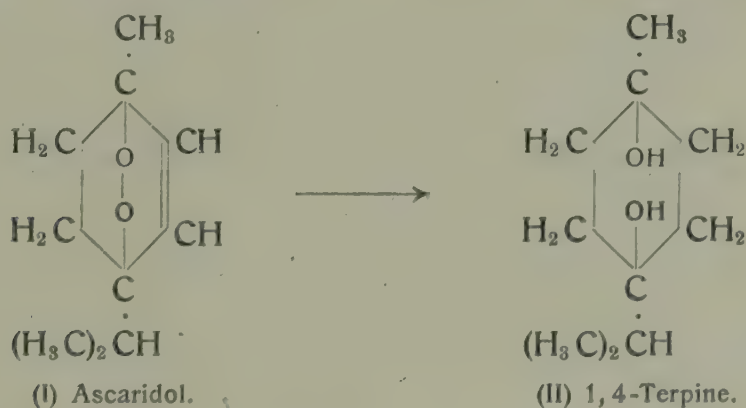
²⁾ Comp. Report April 1907, 142.

³⁾ Comp. Report April 1908, 185.

permanganate. An alcohol $C_{10}H_{19}OH$ (b. p. 207 to 208°; d_{190} 0,9080; n_D 1,4656) was formed, which, when heated with zinc chloride, yields a hydrocarbon, b. p. 173,5 to 175,5° (d_{190} 0,821; n_{D190} 1,4558; mol. refr. found 45,67, calc. for $C_{10}H_{18}$ 45,63). These values agree well with those which might be expected for a menthene, but the body probably consists of a mixture of the two.

The facts related above justify the assumption that ascaridol, under absorption of 4 hydrogen-atoms, affords a 1,4-terpin (II). Assuming that no atomic transposition has taken place during the process of reduction to 1,4-terpin, ascaridol would possess formula I.

Wallach surmises that the acid $C_{10}H_{16}O_6$, m. p. 186 to 187°, obtained by Nelson¹⁾ from ascaridol, does in fact possess the formula $C_{10}H_{16}O_6$ and that it is identical with α - α' -dihydroxy- α -methyl- α' -isopropyladipic acid. But Wallach does not regard Nelson's formulæ for ascaridol and ascaridol-glycol as likely to be correct.



On the anthelmintic action of *American wormseed oil* (*Oleum Chenopodii anthelminthici*), see p. 120.

Oil of Levant Wormseed (*Ol. Cinae*) still remains unobtainable, but it would appear as if the consumers had at length made up their minds to do without the article, enquiries for the oil being now very rare.

Wormwood Oil. According to information gathered by our New York branch the production of American wormwood oil in the States of Michigan and Indiana was about the same this year as in 1911, the total acreage under wormwood being 390 acres in 1912, compared with 385 acres in 1911. There are frequent complaints of sluggish sale, because in some European countries the demand for wormwood oil has been greatly reduced owing to the prohibition of the sale of absinth; and it is thought that the high values of recent years, which, for the rest, have already shown some weakening lately, will soon be a thing of the past. Consumers have consoled themselves for the lack of French wormwood oil all the more

¹⁾ *Loc. cit.*

readily because in our German oil, distilled from herb grown here in Miltitz, we have placed upon the market an article which is able to meet the requirements of every expert. Owing to the increasing sale we have extended our plantations last year and have also been in a position to reduce our price somewhat, as the fields are in excellent condition and will yield an abundant second crop. We also beg to draw attention to our terpenless wormwood oil, which we can thoroughly recommend.

Ylang-Ylang Oil. Generally speaking business in the article was not particularly brisk, but of our well-tried "Sartorius" brand no stock has accumulated here, although the shipments have been plentiful. In the course of many years this exquisite quality has become an indispensable ingredient of a very large number of the specialities of first class perfumery-firms, and has everywhere acquired such a high reputation that even the large and frequent shipments which have lately reached us from Manila have quickly gone into consumption. In Réunion ylang-ylang, however, the position is very different indeed. As we have frequently pointed out, this oil is produced in such large quantities as to make the commercial future of the article very precarious. Last year 1510 kilos were shipped up to the end of June, but in the corresponding period of the present year the exports have risen to 2030 kilos. We understand that one of the principal producers has for some considerable time been engaged in a law-suit with a European firm concerning the acceptance of a parcel of 1100 kilos, which is at present lying in consignment in France. So far as the case has gone at present the decision is in favour of the producer, and it is therefore probable that before long the parcel will have to be disposed of. There is scarcely room for doubt that when this happens the market will suffer considerably.

In an article by R. Stanger¹), on the flowers which yield ylang-ylang and cananga oil we find a detailed botanical description of the parts of the flower of *Cananga odorata*. The article contains several illustrations mostly relating to the anatomy of the flowers examined by the author.

Chemical Preparations and Drugs.

"Agrumi" Oils, synthetic (Italian Essences). The continuation of the high range of values of the Sicilian and Calabrian essential oils (see p. 54), has induced us to place upon the market within the past few months synthetic bergamot oil, synthetic lemon oil and synthetic orange

¹) *Pharm. Post* 45 (1912), 593.

oil. These oils are not only very moderate in price, but they possess all the properties which render them for many purposes fully equivalent substitution-products for the natural oils. Our synthetic bergamot oil, with an ester content of about 38 p.c. (ordinary pure Calabrian bergamot oil only contains about 35 p.c. of ester), is a specially successful preparation, and meets with general approbation. Its appearance upon the market has contributed in keeping the value of genuine bergamot oil to some extent within reasonable limits. We cannot abstain from giving a word of commendation to these excellent substitution-products, of which we shall be glad to supply samples.

Almond Oil, pressed, from Almonds (German Pharmacopœia V).

According to all the reports which are to hand the almond crop in Apulia and Sicily promises to turn out well. If, in spite of this, the prices remain at the same level as before, the principal reason is probably that the producers have lately made good profits out of the article, and are therefore in a position to maintain an attitude of reserve. On the one hand there are no sellers, and on the other there is a lively demand on the part of consumers; in fact, it is said that considerable transactions of new crop almonds for future delivery have already been concluded at high prices. Our fixed almond oil, pressed by ourselves, has undergone no change in price of any kind during the past summer, and under the conditions described above there is no present likelihood of any reduction in the quotation. But if within the next few months larger supplies of almonds should be brought to market than can be disposed of among the consumers, it is probable that the quotations of our oil will also recede. We have already repeatedly pointed out that great caution is necessary when purchasing almond oil. "Cheap" oils are always suspect, and samples of such should be sent to our laboratory for examination before the purchase is concluded.

Almond Oil, pressed, from Apricot kernels. As already pointed out in our last *Report*, the prices of prime quality Damascene apricot kernels had receded to 65 *M* per 100 kilos in the spring, owing to the favourable result of the 1911 crop, and we had already based the selling-prices of our apricot kernel oil upon this figure. Since then the prices have remained unchanged at approximately the same level. More recently also, when it was definitely known that the result of the new crop would not exceed a low average yield, the prices, with the exception of some slight fluctuations, have not on the whole gone beyond the quotation mentioned above. It would appear that the French and Italian traders have supplied themselves very abundantly last year; at any rate in April and May there were still very considerable stocks left over in Marseilles. Of late, France has again come into the market as a buyer, and has thereby given it a somewhat firmer tendency. In view of the low average

yield of the crop to which we have referred, a reduction of prices during the winter is of course hardly to be expected. In California the present year's crop of apricots and peaches appears to have been exceptionally abundant, but in spite of this the price has only fallen to about 80 *M*. For this reason the kernels in question are of no interest so far as our industry is concerned; but owing to their fine appearance they are much liked by the provision-dealers as a substitute for bitter almonds. Favourable offers of Chinese and Japanese apricot kernels have been wanting of late.

Ambergris. In the year 1820 Pelletier and Caventou obtained from ambergris, by extracting it with alcohol, a body to which they gave the name of ambraine. The analytical values of ambraine were not published by Pelletier until 1832, when they were given as follows: carbon 81,74 p. c., hydrogen 13,32 p. c., oxygen 4,94 p. c. Some time ago J. Riban¹⁾ has investigated this body more closely. He had come into possession of a small quantity of ambraine which, in the course of time, had separated out from the alcoholic liquid in a bottle intended for extract of ambergris. The substance, after being recrystallised from alcohol, melted between 82 and 86°. Combustion showed it to possess the formula $C_{23}H_{40}O$. Ambraine constitutes an octobromo-substitution-product $C_{23}H_{32}Br_8O$. Heating with phosphorus pentachloride on the water bath gave rise to a chloro-substitutionproduct $C_{23}H_{35}Cl_5O$. Attempts to estimate the molecular weight of ambraine by the cryoscopic method remained without result.

Benzoin, Siam. We recently received a fresh supply of the finest quality, rich in aroma, and were thus in a position to reduce our price somewhat. We regard the present range of prices as favourable, for there is always a brisk demand for really first-class benzoin, and the quality supplied by us invariably meets with so much favour that our stocks as a rule do not last long.

Benzoin, Sumatra. We always keep a full stock of Sumatra benzoin in large almonds, suitable for perfumery purposes, and which we can recommend. We desire to remind our customers of this fact, as the prices are now favourable.

Benzyl Acetate, free from chlorine (98 to 100 p. c.). This article has fallen a victim to extreme price-cutting, which will probably before long bring about the ruin of this very serviceable preparation. A few firms have made it their business to place upon the market qualities which completely discredit this useful perfume. Such cheap qualities should be carefully tested before use, especially because the percentage-proportion guaranteed by the manufacturers has repeatedly been found not to corre-

¹⁾ *Compt. rend.* 154 (1912), 1729.

spond with the actuality. None of the samples tested by us contained more than 96 p. c. benzyl acetate.

Cinnamic aldehyde. T. Delphin¹⁾ reports on what is truly a very peculiar "improving agent" of cinnamic aldehyde. A sample of cinnamic aldehyde purchased from a German firm showed rather too low a sp. gr. and was therefore not in accordance with the requirements of the Swedish Pharmacopœia. In reply to his protest, Delphin received from the firm concerned a "specially prepared fraction" the addition of which to the cinnamic aldehyde, it was said, would raise its specific gravity. Delphin thought it advisable first of all to examine this product a little more closely, arguing quite correctly that the addition of only a small quantity of pure cinnamic aldehyde would be incapable of sufficiently affecting the sp. gr. of the entire parcel. His suspicion that the "cinnamic fraction" contained a foreign body of higher sp. gr. was confirmed by examination, when it was found that the "fraction" consisted of a mixture of about 1 part cinnamic aldehyde and 3 parts benzyl benzoate. Delphin expresses the matter very courteously and reticently when he describes this manipulation as "very peculiar". Unfortunately the name of the manufacturing firm is not given.

Citral. An opportunity having offered itself this year to lay in supplies of the raw material, lemongrass oil, at advantageous prices, we were in a position to make a reduction in our quotations. Whether this reduction will or will not be of a temporary character cannot as yet be said, as this will depend in the first place upon the demand which is to be expected. We are prepared to submit special offers for large contracts.

According to the *Chemist and Druggist of Australasia* [27 (1912), 271] there is no prospect of any increase in the production of oil of *Backhousia citriodora*, which, as is well-known, contains 95 p. c. citral, and of which the employment as raw material in the manufacture of citral was advocated years ago. The large consignment of this oil which was sent to England at the time has brought a loss to the manufacturer in Queensland and as, moreover, there are great difficulties in the way of procuring labour, the manufacture of the oil will always be restricted within a narrow compass.

Civet. Our well-assorted stock of original horns of different sizes has recently been enriched by a parcel which, in respect of quality, throws into the shade everything we had previously received. Judging by the demand which is already showing itself for this civet, the supply will soon be exhausted. We therefore strongly advise the perfumery trade not to allow the occasion of securing some of this unusually beautiful and aromatic parcel to slip by.

¹⁾ *Svensk Farmaceutisk Tidskrift* 1912, No. 12. Quoted from *Apotheker Ztg.* 27 (1912), 402.

Coumarin. A paper has been published by E. Biilmann¹⁾ on complex mercurial compounds in the coumarin-group, and on the conversion of coumarin into β -methoxymelilotic acid, β -ethoxymelilotic acid, and coumaric ester. We can only quote the reference here.

Eucalyptol. H. Brüning²⁾, by experiments with children suffering from ascaridæ, has established the fact that in spite of suitable dosage and administration, eucalyptol (cineol) is wholly ineffective as an anthelmintic. Even when given in comparatively small doses to child-patients it caused abdominal pains, nausea, and vomiting, and even in large doses it failed to have any effect upon the ascaridæ. This experience establishes as a fact³⁾ the surmise which had already been expressed that eucalyptol given in conjunction with chloroform and castor oil, owes its anthelmintic properties solely to the presence of chloroform. After the experiments on animals which had been made by Brüning it was to be foreseen that eucalyptol would prove inactive. Living ascaridæ derived from human beings were not killed by being immersed for several days in a 0,05 p. c. solution of eucalyptol and common salt. The introduction of eucalyptol into the dorsal lymphatic glands of frogs, and also the inhalation of eucalyptol by frogs, only produced passing paralysis. Eucalyptol, given in doses of about 1 cc. per kilo weight of the animal, was not always fatal to toads, complete recuperation taking place in many cases after a narcosis lasting about 40 hours. In the case of fishes, the addition to the water of 1:10000 of eucalyptol did not prove fatal, but the fish were killed by an injection of 0,3 p. c. of their weight of eucalyptol, although an injection of 0,02 p. c. of the weight failed to cause the slightest symptoms of discomfort. Administered to fowls in the proportion of about 3 cc. per kilo weight of the bird, eucalyptol only produced a slight irritation of the bowels. Rabbits and guinea pigs are able to support fairly large quantities of eucalyptol. Brüning has also investigated the action of eucalyptol upon blood, milk, and bacteria. Only in minimum quantities of 4,8 p. c. is eucalyptol able to prevent the development of sulphuretted hydrogen which takes place in the milk-sulphur method⁴⁾, and it is unable to arrest the development of *bacterium coli* and staphylococci even in a strength of 1:20.

When using American wormseed oil (*Oleum Chenopodii anthelminticum*) as an anthelmintic Brüning invariably obtained good results. According to his experience the oil may also be administered with good effect in the form of an emulsion (so-called "wermolin").

In conclusion we present below a table drawn up by Brüning in which the difference between the action of eucalyptol and of American wormseed oil is clearly shown: —

¹⁾ *Liebigs Annalen* 388 (1912), 259.

²⁾ *Zeitschr. f. experiment. Pathologie u. Therapie* 11 (1912), 154.

³⁾ *Comp. Report* April 1911, 121.

⁴⁾ See p. 134 of this report.

American Wormseed oil
(*Oleum Chenopod. anthelm.*)

Eucalyptol

For frogs:

fatal dose about 0,3 p. m. With
0,1 p. m. paralysis.

With 0,2 p.m. weight: paralysis.

For fishes:

With 1: 8000 death,
1:12500 compl. narcosis,
1:25000 stupor.

1:10000 no disturbance.

With fowls:

With 0,5 p.m. giddiness, para-
lysis and death.

3,0 p.m. diminished appetite, bird
remains alive.

With guinea pigs:

fatal dose 0,4 p.m.

In most cases much larger doses
(1 to 2 p.m.) given internally and
hypodermically were supported.

With rabbits:

0,3 p.m. paralysis and death.

Up to 8 g. in 3 days no effect what-
ever; single doses of 5 g. ditto.

Prevented:

Curdling of milk with 1,0 p.c.

With 1,2 p.c.

Evol. of H_2S from milk with 1:50.

With 1:20.

Development of *Bacterium coli* with
1:20 (arresting action up to 1:250).

With 1:20 arresting action only.

With living ascaridæ, 1:10000 kills
within 1 minute.

Kept for several days in 1:2000
without injury.

Geraniol. In view of the high prices of rose oil and of the scarcity of all geranium oils, the demand for geraniol has at times been so extraordinarily brisk that we were compelled, in the case of numerous large orders, to stipulate for a commensurate term for delivery. Finally we were enabled, by increasing our manufacturing plant, to overcome all obstacles, and in the future we will therefore have no difficulty in supplying any desired quantity within the shortest possible time. It is a well-known fact that we require our geraniol to stand the highest tests in respect of quality, and this is precisely the reason why our sales of this important perfume have so enormously increased during the last few years.

Linalyl acetate. A case came before us recently to which we wish to refer in some detail here as showing what kind of products are occasionally brought into commerce under the name of linalyl acetate.

A product, originally derived from a Leipzig firm, and submitted for our opinion by a third party, was examined with the results set forth below. For purposes of comparison we add the properties of a preparation prepared by ourselves and actually containing 80 p. c. of linalyl acetate:

	Sample under exam.	80 p. c. linalyl acetate Schimmel & Co.
d_{150}	0,9207	0,90 to 0,91
α_D	+ 0° 38'	According to the rot. of linalool used, to the right or left.
n_{D20}	1,46360	1,451 to 1,454
Esters (calc. on the basis of linalyl acetate) about	81 p. c.	about 80 p. c.
Soluble in	6 vols. a. m. 70 p. c. alc.	3 to 5 vols. a. m. 70 p. c. alcohol.

Fractional Saponification¹⁾:

Ester v. after 2 hours' sap. with 40 cc. seminormal potash liquor	242,5	} Under fract. saponific. differences ranging from 0,7 to 5,8 were observed.
Ester v. after 1 hour's sap. with 20 cc. seminormal potash liquor + 25 cc. alcohol	206,5	
Difference	36,0	

The above table clearly shows the great difference between the two products. The sp. gr. and the co-efficient of refraction of the sample were too high, its solubility was somewhat less and the difference in fractional saponification was much too great. The last-named value pointed to a high terpinyl acetate content, a suspicion which was confirmed by the odour of the sample. The behaviour on boiling afforded another proof of its abnormal character. For whereas linalyl acetate boils between 79 and 81° at 4 to 5 mm. press., only 6,9 p. c. of the sample in question passed over at that temperature, 5,4 p. c. passing over between 81 and 89°, and 71,8 p. c. between 89 and 98°. Closer examination of the separate fractions showed that the preparation contained only very little linalyl acetate and that it consisted chiefly of terpinyl and geranyl acetate. The non-esterified portions consisted in part of hydrocarbons.

After this result it was obviously impossible to pronounce a favourable opinion. The manufacturer, we were informed, had given an assurance that there was no question of any adulteration, and we must therefore describe the preparation as a complete failure from the point of view of

¹⁾ Comp. Report October 1911, 116.

manufacture. The esterification of such an unstable body as linalool demands special precautions, failing which, as was shown by the case under discussion, the final product is something quite different. At the same time we wish to correct the somewhat hasty assertion of the firm which had supplied the product to the effect that we, too, were unable to prepare linalyl acetate free from geranyl-, neryl-, and terpinylacetate and that the 80 p. c. referred to by us was merely meant to indicate the total ester-content. In reply to this assertion we declare that the linalyl acetate prepared and placed upon the market by us consists exclusively of linalool and linalyl acetate and contains on the average 80 p. c. of the latter.

Menthol. In accordance with our custom we deal with this article under the heading "Peppermint oil, Japanese", see p. 90.

Musk, Tonquin. According to reports received from our informants in Shanghai the present year's musk-season, which was only opened in May, has been of brief duration. Unfortunately the conditions of the musk-trade still remain without improvement, for the scene of the hostilities between the Chinese and Tibetans which have now been in progress for some time lies partly in the musk-districts between Sze-chuen and Thibet. If higher prices have to be paid the principal reason is the brisk demand for musk from America, France and England, for the insecure conditions prevailing in the interior of China are naturally an inducement to the musk-hunters to send the results of the chase to the coast with all possible dispatch, as it is too risky to store the musk in the unsettled districts. The above information would really lead to the conclusion that stocks are being accumulated in Shanghai.

Peru Balsam. As always, it is difficult to fathom the commercial position of this article and we must therefore restrict ourselves to place upon record the fact that during the summer the prices have generally remained unaltered. The leading importers at the present time show a firm attitude, and all hope of an early return to low prices would therefore seem to be vain.

According to A. Hale¹⁾, San Salvador exports annually about 130000 pounds (gross) of Peru balsam, of which 65000 pounds are sent to Germany. Recently the Government of the Republic has placed an export duty of 1 Peso (about 40 cents gold) per quintal gross (101,4 pounds) upon Peru balsam.

Quino-Quino balsam. In a previous *Report* (April 1910, 149), we published a brief reference to this balsam, taken from a paper by Hartwich and Jama. A balsam derived from the same plant (*Myroxylon*

¹⁾ *Americ. Perfumer* 7 (1910), 10, 40.

Balsamum var. γ *punctatum*) has now also been described by J. D. Riedel¹⁾, who states that it possesses the following properties:

A thick sticky extract, with an odour of coumarin, which, when exposed to air, dries up into a soft, friable resin. Saponification number 184,8. A constituent corresponding to the cinnaine of Peru balsam, of which the extract yielded 10,1 p. c. was of semi-solid consistency and had sap. v. 99,9.

This description does not quite tally with that of Hartwich and Jama, inasmuch as the balsam examined by the latter was solid, had an odour of tolu balsam, and yielded 5,83 p. c. of a cinnaine of oily consistency, which only solidified into an ointment-like mass at -20° . The sap. v. of this balsam was 134,09. It is also noteworthy that the product analysed by Riedel contained no cinnamic acid, whereas Hartwich and Jama were able positively to identify cinnamic acid in their balsam. The difference in the consistency of the two balsams Hartwich and Jama²⁾ regarded as an accident, and the other differences they attribute to the fact that Riedel's balsam was not, like theirs, obtained from an incision in the trunk of the tree, but probably from the fruit. They support this theory by pointing out, among other things, that the conditions in the case of Peru balsam are quite similar, for there, too, the fruit yields a product with an odour of coumarin, and free from cinnamic acid. Moreover, from the examination of a sample of the balsam sent to them by Riedel they found that the odour reminded less of coumarin than of piperonal, but they leave it an open question whether the last-named body or, possibly, vanillin is present in the balsam.

Rose "Schimmel & Co." (Red Rose). As already pointed out in another part of this *Report*, the present year's rose-gathering in our extended plantations at Miltitz has been carried out under very favourable conditions, and we have therefore been able to prepare a sufficient quantity of the natural raw material of our speciality, although by doing so we used up the greater part of our flower-output, so that it was only possible to distil small quantities of rose oil. Our "Red Rose Schimmel & Co." has continued to pursue its victorious career in the perfumery-industry, and the extent of its sale within recent months borders upon the incredible. In the course of the last few years we have successfully placed upon the market many interesting novelties in the domain of odoriferous substances, but we are once more able to declare that no other similar speciality has even approximately gained such a measure of approbation as has fallen to this rose-perfume with a natural basis during the brief period which has elapsed since its introduction. Our "Red Rose" represents a brilliantly successful blending of Nature and Art.

¹⁾ *Riedels Mentor* 1912, p. 33.

²⁾ *Schweiz. Wochenschr. f. Chem. u. Pharm.* 50 (1912), 312.

Safrol. We continue to manufacture safrol upon the largest imaginable scale, and as we are consequently in a position to utilise to the full all the advantages of an extensive plant, we are able to make very advantageous offers of this article, which not only forms the raw material of a whole series of synthetic perfumes, but also occupies a prominent position in soap-manufacture and in the preparation of numerous technical products. If we maintain our prices, the reason is that in spite of our enormous output we are scarcely ever able to accumulate stock, the demand generally exceeding the capacity of our plant.

Storax. To test the purity of storax, C. Ahrens¹⁾ makes use of its property of being partly soluble in light petroleum. After freeing the balsam under examination as far as possible from its adherent water by means of filtering paper, Ahrens levigates from 4 to 5 g. (exactly weighed) with about the same quantity of washed-out sand. The mixture is then kneaded in a triturating-dish with light petroleum (b. p. 70°; $d_{15} 0,65$), constantly renewed, until the light petroleum ceases to absorb any soluble matter. Owing to the toughness of the mass this kneading-process is a little troublesome at first, but when the mass has been worked up several times with benzine it gradually begins to crumble and finally to powder and then is readily levigable. The entire extract of light petroleum (totalling from 350 to 400 cc.) is filtered in two separate portions into a tared wide-necked flask of about 250 cc. capacity, the light petroleum being distilled off on the water bath as far as possible. The flask is then placed on a heated oven for the purpose of removing the last traces of the light petroleum, a manipulation which can be hastened by spreading the contents at the walls of the flask. The drying is continued until constancy of weight is attained; this detail being checked every quarter of an hour.

When the storax is pure the residue thus obtained is pale yellow, extremely viscous, possessing an agreeable odour and strongly refractive of light. A pronounced adulteration with colophony is indicated by a dark colour and by the fact that the residue has ceased to be fluent.

For further examination of the storax the determination of the acid and saponification values of the light petroleum extract is recommended. The residue is dissolved in about 30 cc. of cold, neutral 95 p. c. alcohol, and the solution is first neutralised with alcoholic seminormal potash liquor to determine the acid value. The ester value is estimated by adding a further 25 cc. of potash liquor, leaving the well-closed flask to stand for 24 hours and titrating back the unconsumed liquor with seminormal sulphuric acid.

In the course of testing a series of storax samples, Ahrens obtained a light petroleum extract varying from 37,6 to 47,7 p. c. of the original

¹⁾ *Zeitschr. f. öff. Chem.* 18 (1912), 267. Quoted from *Apotheker Ztg.* 27 (1912), 651.

drug¹⁾. In his view a good commercial storax should contain from 37,6 to 56 p. c. constituents soluble in light petroleum. The acid values of the light petroleum extracts estimated by him ranged from 36,6 to 62,9, the saponification values from 193,9 to 199,6.

For estimating the percentage of water in storax the author recommends the following indirect method, which is said to be more accurate than the usual direct method of estimation: an exactly weighed quantity (4 to 5 g.) of storax is rubbed up in a tritulating dish with a little anhydrous sodium sulphate and ether; the ethereal solution is filtered through a tared filter into a flask of 100 cc. capacity; the dish and the filter carefully washed out with ether and the filtrate made up to 100 cc. The ethereal solution is then left to stand for several hours over a little anhydrous sodium sulphate; after which 50 cc. of it is evaporated in a tared flask and the evaporation residue dried until there is no further loss in weight. The filter mentioned above is then also dried, the sodium sulphate having previously been removed by washing with water. The loss in weight as compared with the original weight of the storax represents the water-content of the drug.

For detecting adulteration with olive or castor oil, a form of sophistication which is also frequently practised, the iodine-value is said to be useful.

For the quantitative assay of cinnamic acid in storax balsam, C. A. Hill and T. T. Cocking²⁾ saponify 2,5 grams balsam by boiling for one hour with 25 cc. seminormal alcoholic potash and 20 cc. alcohol. The alcohol is then evaporated and the saponified mass dissolved in 50 cc. water. The aqueous solution is shaken with 20 cc. ether, allowed to stand, the ethereal layer separated, washed with 5 cc. water and the washings mixed with the remainder of the aqueous solution. The aqueous solution is next acidified and shaken out with ether four times. The ethereal extract is washed with water, after which the ether is distilled off and the residue boiled vigorously for 15 minutes on a reflux condenser with 100 cc. water. The cinnamic acid is deposited in the cold from the filtrate of the separated cinnamic acid and this treatment is repeated until no more cinnamic acid goes into solution. The acid, collected upon a filter, is pressed and either dried over sulphuric acid and weighed or titrated in alcoholic solution with decinormal sodium hydroxide. As the cinnamic acid is to some degree soluble in water, 0,03 g. is added to the result obtained. By this method samples of good quality storax were found to contain from 21,6 to 30,68 p. c. cinnamic acid.

¹⁾ E. Dieterich found that from 15,0 to 19,4 p. c. of crude storax is soluble in light petroleum. Comp. K. Dieterich, *Analyse der Harze, Balsame und Gummiharze*. Berlin 1900, p. 188.

²⁾ *Chemist and Druggist* 80 (1912), 412.

Thymol. The prices of thymol have at length improved a little, and have acquired a reasonable relation to the cost-price of the raw material (ajowan seed), of which the quotation this year is about 11/-. Since the Hamburg firm which was chiefly responsible for the demoralisation of the thymol trade in recent years has abandoned the manufacture, business in this important preparation has again assumed a more pleasant aspect. We have long foreseen the commencement of this reversal in the thymol market and, as is well known, we have never taken any part in the measureless price-cutting which unfortunately has been a feature of the article in the last few years.

Tolu Balsam is very scarce. It would appear as if the upward movement in prices which set in in this article a few months ago has not yet attained its limit. Our purified quality especially has been in great request on the part of the perfumers.

Vanillin. The effect of the action of light upon vanillin in benzene, toluene and other solvents has been investigated by E. Puxeddu¹⁾ In every instance the splitting-off of 2 hydrogen atoms from 2 molecules of vanillin resulted in the production of dehydrovanillin (m. p. 305°), together with vanillin alcohol. The methyl or ethyl ethers of vanillin behave very differently; here there results an acid, 2 molecules of the ether first condensing and the product of condensation reacting with fresh ether. It has been found impossible to isolate the intermediate bodies from the reaction-mixture; nothing but the acid was obtained in any of the experiments.

In the same manner methylvanillin yielded methylvanillic acid (m. p. 177°) and ethyl vanillin, ethylvanillic acid (m. p. 195 to 196°).

¹⁾ *Atti R. Accad. dei Lincei*, Roma (5), 20 (1911), II. 717. Quoted from *Chem. Zentralbl.* 1912, I. 724.

Notes on Scientific Research in the Domain of the Essential Oils.

General.

Part 12 of the *Zeitschrift für das Landwirtschaftliche Versuchswesen* (1911) contains an article by W. Mitlacher on experiments in the cultivation of medicinal plants to which we have already referred in our *Report* of April 1911, p. 147. A more detailed second edition of this work has appeared in the *Zeitschrift des allgemeinen österreichischen Apotheker-Vereins* [Vol. 50 (1912), p. 347, 357, 367, 375, 383, 391, 399, 409].

With the object of determining the solubility of water in essential oils, J. C. Umney and S. W. Bunker¹⁾ have shaken up with water a number of essential oils, the sp. gr. and the refractive index being determined both before and after the treatment. The percentage of water contained in the oil may be readily calculated from the difference of the two values above referred to. A more accurate result is obtained by passing steam into the oil-samples and by determining the refraction and the sp. gr. before and after this manipulation. Every decrease in the index of refraction by 0,0001 indicates the presence of 0,07 to 0,08% water. Generally speaking, the oils which consist of terpenes, oxides, or ketones absorb no water, whereas distillates containing alcohols or phenols absorb water fairly freely. The values ascertained by the authors for the principal oils are reproduced in the table (p. 129).

Bibliography.

W. Müller²⁾ has published an article on progress in the domain of the chemistry of the terpenes and odoriferous substances.

P. Jeancard and C. Satie deal in the *Revue générale de chimie pure et appliquée* [Vol. 15 (1912), p. 289] with the new work published in the year 1911 in the domain of the chemistry of perfumery.

The literature of the chemistry of volatile oils and odoriferous substances has been enriched by a new work, namely, E. Charabot's "*Les principes odorants des végétaux (Méthodes de dosage, d'extraction, d'identification)*" (Paris, 1912, pp. 388). The author, in 9 chapters, deals with the majority

¹⁾ *Perfum. and Essent. Oil Record* 3 (1912), 101, 197.

²⁾ *Fortschritte der Chemie, Physik und physik. Chemie* 6 (1912), 45.

Table showing percentage of water absorbed by various essential oils.

Oil	$n_{D_{25}^o}$		Difference	Water p. c.
	of the dry oil	of the moist oil		
Anise oil	1,5506	1,5506	0	0
Bergamot oil	1,4634	1,4631	0,0003	0,26
" "	1,4634	1,4634	0	0
Bitter Almond oil	1,5388	1,5373	0,0015	0,70
Cajuput oil	1,4649	1,4647	0,0002	0,16
Cananga "	1,4990	1,4989	0,0001	0,06
Caraway "	1,4847	1,4847	0	0
Cassia "	1,6003	1,5999	0,0004	0,14
" "	1,6003	1,6003	0	0
Cedarwood oil	1,5011	1,5010	0,0001	0,06
Cinnamon bark	1,5714	1,5714	0	0
Citronella oil	1,4770	1,4769	0,0001	0,07
" "	1,4790	1,4790	0	0
" " Java	1,4660	1,4659	0,0001	0,08
" " "	1,4660	1,4660	0	0
Clove oil	1,5300	1,5295	0,0005	0,24
" "	1,5300	1,5299	0,0001	0,05
Eucalyptus oil, Globulus	1,4602	1,4600	0,0002	0,17
" " "	1,4602	1,4602	0	0
Gaultheria "	1,5329	1,5329	0	0
Geranium " French	1,4638	1,4638	0	0
Juniper oil	1,4785	1,4785	0	0
Lavender " Mitcham	1,4629	1,4625	0,0004	0,34
Lemon oil	1,4729	1,4729	0	0
Lemongrass oil	1,4824	1,4820	0,0004	0,29
" "	1,4824	1,4823	0,0001	0,07
Linaloe oil	1,4625	1,4619	0,0006	0,52
Neroli oil	1,4693	1,4689	0,0004	0,33
Orange oil	1,4715	1,4715	0	0
Patchouly oil	1,5072	1,5067	0,0005	0,20
Petitgrain "	1,4623	1,4623	0	0
Peppermint oil, America	1,4602	1,4600	0,0002	0,16
" " Japan	1,4583	1,4581	0,0002	0,16
" " Mitcham	1,4597	1,4597	0	0
Rosemary "	1,4672	1,4672	0	0
Sandalwood oil	1,5038	1,5035	0,0003	0,17
" "	1,5038	1,5038	0	0

of the constituents of essential oils. He mentions the distribution, chemical and physical properties and the tests for the detection of the bodies in question and, in conclusion, gives a welcome bibliography of the principal books and periodicals dealing with essential oils and odoriferous substances.

Under the title "*De l'embaumement avant et après Jésus Christ*" L. Reutter has published a book in which he not only describes the materials employed in embalming but also gives detailed information on the manner in which embalming is carried out.

The same author has dealt experimentally with part of a paper by A. Tschirch²⁾ on the resins employed in Egypt and Carthage for embalming corpses in the ten centuries preceding the Christian Era. Among others he has examined the mummy of the Hekan-M-Saf, commander of the Egyptian Navy at the time of the 30th Dynasty. The presence of storax, mastix, Aleppo resin, and asphaltum was demonstrated, that of Chio turpentine and cedarwood resin was uncertain. Similar results were obtained from the examination of an embalmed ibis in the Museum of Neuchâtel. In addition to storax and asphaltum, a tar was found to be present which yielded benzene and phenol. The ibis-mummy further contained a resin yielding an essential oil from which colourless crystals, m. p. 96°, were precipitated. The author also investigated the contents of an urn, in which he found a resin showing a close resemblance to gurjun balsam. Resin collected from the sarcophagus of a priest of the necropolis of Carthage was found to contain mastix, storax, and Aleppo resin, also most probably sandarach and asphaltum. The resin was scented; when subjected to steam-distillation it yielded a volatile oil containing thymol. Another resin obtained from Carthage showed a similar constitution except that, besides the ingredients above mentioned, it contained incense. This product was also scented and afforded an oil in which the presence of thymol was demonstrated.

"*Commercial Guide to the forest economic products of India*" is the title of a book by R. S. Pearson³⁾ which contains valuable data on many oil or balsam-yielding trees of the Indian forests. It includes articles on the sandal tree, *Pinus excelsa*, Wall ("Blue Pine") and *Pinus longifolia*, Roxb. which are well worth attention. The oil grasses (*Cymbopogon* species) are also mentioned, as well as various other products, including camphor, cinnamon, gurjun balsam (from *Dipterocarpus turbinatus*, Gaertn. f.) cardamoms, &c. Mr. Pearson, however, deals chiefly with the economic woods, to which we are unable to refer here.

¹⁾ Paris and Neuchâtel. From a copy kindly sent to us.

²⁾ *Arch. der Pharm.* 250 (1912), 170.

³⁾ Calcutta 1912.

⁴⁾ See the present *Report*, p. 106.

Analytical Notes.

For purposes of the quantitative determination of aldehydes and ketones, F. de Myttenaere¹⁾ has endeavoured to make use of their property of combining with hydrocyanic acid, forming cyanohydrines. He has, in part, obtained practicable results. The estimation is carried out as follows: the compound in question was diluted with hydrocyanic acid in an aqueous or a faintly alkaline solution, in the proportion of about 1 molecule of aldehyde or ketone to 4 molecules hydrocyanic acid. The dilution had been arranged so that 100 cc. of the liquid should contain about 0,4 grams hydrocyanic acid. The mixtures were first heated for 75 minutes on the water-bath in a sealed flask and afterwards left standing for 12 hours at room temperature. After this the total and the still remaining free hydrocyanic acid were determined and the acid in combination with the aldehyde or ketone was calculated from the difference; the proportion represented by the compounds which had entered into reaction being calculated in turn from the data thus obtained.

De Myttenaere estimates the total hydrocyanic acid by the following method: exactly 6 cc. of the solution to be tested is added to 75 cc. water; 10 drops of 40 p. c. soda liquor, 10 cc. 17 p. c. ammonia solution, and finally a few drops of a 10 p. c. solution of potassium iodide is added and the mixture titrated with centinormal silver solution. To determine the free hydrocyanic acid, the author adds to 50 cc. centinormal silver solution, placed in a measuring flask of 100 cc. capacity, exactly 3 cc. of the solution to be tested, shakes, adds water to 100 cc., filters, and estimates in 50 cc. filtrate the excess of silver nitrate with centinormal ammonium sulphocyanide, ferri-ammonium aluminate being used as an indicator.

The author has obtained good results with the lower fatty aldehydes as well as with benzaldehyde, but the method failed with citral, vanillin, and dextrose, and also with ketones.

On the estimation of citronellal in citronella oil see p. 40.

According to A. Seidell²⁾, the estimation of thymol may be carried out as follows: 0,1 to 0,5 grams thymol is placed in a flask of 300 cc. capacity with 1 to 2 cc. carbon tetrachloride and 100 cc. water. Bromine vapour is then poured into the mixture so long as the brown colour persists after shaking. After 30 minutes 5 cc. carbon disulphide, and immediately afterwards an aqueous 20 p. c. potassium iodide solution in excess are added to the liquid. The liberated iodine is titrated with decinormal thiosulphate solution. After this, 2 p. c. aqueous potassium iodate solution is added and the iodine set free is again titrated. The thiosulphate which is used up in the second titration corresponds to the

¹⁾ *Annal. de Pharm.* 18 (1912), 1.

²⁾ *Americ. chem. Journ.* 47 (1912), 508. From a copy kindly sent to us.

quantity of thymol employed. 1 cc. decinormal thiosulphate solution
= 0,007506 grams thymol.

On the estimation of cinnamic acid in storax balsam see p. 126.

Physical Notes.

As stated on p. 160 of our *Report* of April 1912, Hantzsch regards the absorption-method as much more sensitive than the refraction method which is employed by Auwers for constitutional determinations. Auwers disputes this and many other assertions of Hantzsch. Auwers holds that it is unnecessary first to fractionate *in vacuo* the terpene hydrocarbons of which the spectrochemical properties are to be examined, as is done by Hantzsch, and he believes that distillation at ordinary pressure is sufficient. While not at all doubting the great sensitiveness of the absorption-method, Auwers believes that it is still very questionable whether by that method it is possible to obtain the same definite information concerning questions of chemical constitution as by the refraction-method. It is not yet possible to say whether there is any prospect of such definite information being afforded by the absorption-method, inasmuch as extensive systematic investigation is needed to answer the question.

Soon afterwards a reply by Hantzsch²⁾ made its appearance, from which we will only abstract the points which apply to our particular industry. In reply to a question by Hantzsch, Wallach has informed him that although he regards it as desirable to state the boiling-point of the terpenes at ordinary pressure, when it was a question of obtaining the body in the pure state and of determining its constants, he has always proceeded by distillation *in vacuo*, and has laid stress upon the liability to change of, say, pinene, phellandrene, terpinene, &c., when distilled under ordinary pressure.

In our last *Report*³⁾ we mentioned some papers by Golodetz⁴⁾ on "New methods for the separation of mixtures with closely approximating boiling-points, and of mixtures which boil without decomposition", and we then stated that we intended eventually to return to the subject later on. Now that Golodetz's publication is before us in its entirety, such further reference would be superfluous, seeing that those parts of the work which interest us, but with which we were already familiar, have already been dealt with in their essential points in another publication by Golodetz⁵⁾ to which we referred at the time⁶⁾. We have nothing to add to the particulars which we then gave.

¹⁾ *Berl. Berichte* 45 (1912), 963.

²⁾ *Ibidem* 1742.

³⁾ *Report* April 1912, 156.

⁴⁾ *Chem. Ztg.* 36 (1912), 273, 297, 302.

⁵⁾ *Journ. Russ. phys. chem. Soc.* 43 (1911), 1041. Quoted from *Chem. Zentralbl.* 1912, I.

⁶⁾ *Report* April 1912, 153.

E. Deussen¹⁾ has worked out a method which — as he says himself — is based on limited experimental material only and which makes it possible in several, if not in many, cases to test the purity of optically active substances. He examined β -caryophyllene nitrosite, caryophyllene glycol, caryophyllene nitrolanilide, and cadinene hydrochloride, taking two preparations of different m. p. of each compound. As sources of illumination he employed sodium-light of 589 $\mu\mu$ and mercury-light of 491 $\mu\mu$. He tested β -caryophyllene nitrosite, m. p. 115 and 113,5° (the second sample being therefore impure) and determined the specific rotation of different concentrations of each of these two samples, doing the same with the other compounds. These investigations showed that the impurities or admixtures contained in the nitrosite and glycol are optically active, whereas those contained in the nitrolanilide are in all probability inactive.

It would lead us too far here to discuss also the other peculiarities mentioned by the author in the course of his comments on his tables, in particular because it is extremely difficult properly to judge the values given. This is perhaps due in part to the fact that the various compounds have been taken in very different concentrations.

In conclusion the author observes that his method is also serviceable in the testing of terpene derivatives, alkaloids, albuminous substances, and similar bodies.

Deussen has brought together the result of his observations in the form of 4 tables. In perusing these tables he has arrived at the conclusion "that the result not only claims to be of special, but also probably of general, interest".

On the action of light upon *isoeugenol* and upon *vanillin* see pp. 162 and 127.

Pharmaco-physiological Notes.

Several investigators have recently been engaged in exploring the disinfecting and narcotic action of the essential oils and their constituents. In our *Report* of April 1911, p. 157, for example, we discussed a paper by W. H. Martindale on the antiseptic action of essential oils, and in our *Report* of October 1911, p. 123, we referred to a publication by Coupin on the influence of certain volatile bodies on the development of germinating grains of cereals. In our *Bericht* April 1911 we published, as a supplement, an article by R. Geinitz on the action of Δ^1 -p-menthenone-3, a body the presence of which in Japanese peppermint oil had been detected by us. The last-named author has since published a paper under the title "Vergleichende Versuche über die narkotischen und desinfizierenden Wirkungen der gangbarsten ätherischen Öle und deren wirksamen Bestandteile"

¹⁾ *Journ. f. prakt. Chem.* II. 85 (1912), 484.

(comparative experiments on the narcotic and disinfecting action of the most frequently-used essential oils and of their active constituents)¹⁾, and to this work we desire briefly to refer.

The principal outcome of Geinitz' investigations is the establishment of the fact that the narcotic and disinfecting properties of the essential oils do not correspond with those of the active constituents of those oils; the sequence of the series differs widely. For example, Russian anise oil and its active constituent, anethol, have no antiseptic action whatsoever, but both have a pronounced narcotic action upon cold-blooded animals. It would appear that the group which exerts an antiseptic action and that which acts narcotically are not found in the same molecule of the odoriferous bodies; nay, in many of these substances one of the groups is wanting altogether. It is also necessary to abandon the theory that narcosis is determined simply by the great solubility of lipid in the cells of the nervous system, and that the antiseptic action of essential oils depends upon solubility of the bacteria in the lipoids. The explanation of the facts which have been observed is probably that the organism of the bacteria with its peculiar metabolic process occupies in Nature a position wholly for itself. For the results of narcotic experiments which have been obtained with essential oils in the case of cold-blooded animals and in that of the higher plants are altogether different from those which have been obtained with bacteria.

The results of narcotic experiments with fishes and tadpoles, of respiration-experiments with toads, and of injection-experiments with frogs, are reproduced in the form of tables arranged according to the degree of activity of the essential oils.

For the purpose of testing narcotic action on fishes, roach (*Leuciscus rutilus*) were used. The limit of concentration taken was the dilution which produced perceptible narcosis in the fish within a period of 24 hours, that is to say, a condition when the animal, without displaying much spontaneous motion, floated in the water in an atactic condition and altogether failed to respond to squeezing with hooked pincers. Only those experiments were regarded as affording proof in which the fish recovered when replaced in fresh water.

For the purpose of estimating the antiseptic action, Geinitz added in each case to 10 cc. fresh milk, placed in a test tube of 16 to 18 cc. capacity, first as much *Sulphur depuratum* as would lie on the point of a knife, and afterwards the antiseptic. After vigorous shaking a piece of filtering-paper soaked with solution of lead acetate was hung up in the upper part of the test-tube in such a way as not to come in contact with the milk, and the test-tube was closed with a wad of cotton-wool. The tubes were then

¹⁾ Copy from the *Sitzungsberichte und Abhandlungen der naturforschenden Gesellschaft zu Rostock*, New Series, Vol. IV, 1912. Rostock 1913. The paper was awarded a prize.

kept 24 hours in a water plug-bath at about 38°. If, after that lapse of time, the lead-paper was found to be blackened, it was evident that the tube in question did not contain a sufficient proportion of the antiseptic. As a series of test-tubes was always being treated with an increasing quantity of antiseptic, it was easy to determine exactly when the limit of concentration was reached at which the activity of the bacteria was impeded¹⁾.

Experiments in narcosis, made on fishes.

Substance	Dilution	Substance	Dilution
Mustard oil (allyliso-sulphocyanate)	1:1 320 000	Fennel oil	1 : 34 535
Cinnamon oil	180 000	Terpineol (liquid)	32 000
Citral	153 846	Coumarin	28 571
Carvacrol	134 010	Turpentine oil, fraction containing β -pinene	28 000
Thyme oil	133 333	<i>d</i> - α -Pinene	26 806
Carvone	125 918	Borneo camphor	26 087
Sandalwood oil	116 327	Eucalyptol (Cineol)	22 000
Eugenol	111 836	<i>l</i> - α -Pinene	20 105
Anethol	104 587		
Greek turpentine oil	86 405	Benzaldehyde	18 096
French " "	79 493	Oenanthal	16 788
Spanish " "	77 304	Menthenone	16 000
American " "	77 304	Umbellulone	15 000
Calamus oil	71 862	Eulimene (artificial limonene)	13 000
German peppermint oil	70 000	Rosemary oil	13 333
Russian anise oil	67 000	Juniperberry oil	11 320
Clove oil	67 000	Cymene	10 965
Mitcham peppermint oil	66 666	Terpineol (cryst.)	10 554
Caraway oil	62 500	Anisic aldehyde	10 164
Safrol	60 560	Lemon oil	9 157
		Chloroform	8 070
Heliotropin	45 454	Fenchylisovalerate	6 345
Heptyl alcohol	45 000	Bornylisovalerate	6 300
Rose oil	41 715	Limonene	1 040
Lavender oil	38 764		
Mace oil	38 527	Chloral hydrate	286
Octyl alcohol	38 090	Alcohol	190
Geraniol	37 500	Ether	166

¹⁾ The evolution of sulphuretted hydrogen from milk diluted with sulphur is due to bacterial action.

Antiseptic milk experiments.

Substance	Dilution	Substance	Dilution
Potassium silver cyanide	1:10000	Lavender oil	1 : 28,67
Corrosive sublimate . . .	7000	Cenanthol	27
Mustard oil	2696,7	Spanish turpentine oil .	23
Cinnamon oil	987,77	Caraway oil	20,83
Tricresol	438	Rose oil	17,4
Hydrogen peroxide . . .	332	Borneo camphor	14,5
Anisic aldehyde	170	Mace oil	12,92
Phenol	160	<i>l</i> - α -Pinene	11,7
Ortho-, meta- and para- cresol	143	Juniperberry oil	8,7
Octylalcohol	127	Lemon oil	8,14
Carvacrol	111,7	Sandalwood oil	7,75
Heptylalcohol	100	Americ. turpentine oil . .	5,64
Eugenol	93	French " "	5,64
Menthenone	92,9	German peppermint oil .	5,5
Benzaldehyde	90,72	Mitcham " "	5,5
Coumarin	99,3	Rosemary oil	5,5
Clove oil	74,56	Fennel oil	5,1
Umbellulone	74	Geraniol	3
Greek turpentine oil . . .	72	Russian anise oil	No effect
Heliotropin	64	Anethol	
Turpentine oil fraction containing β -pinene . .	56	Bornylisovalerate	
Terpineol (cryst.)	56	Fenchylisovalerate	
Carvone	54,5	Calamus oil	
<i>d</i> - α -Pinene	44,6	Citral	
Terpineol (liquid)	42,6	Collargol	
Antiformin	40,26	Cymene	
Heptin	37	Eulimene	
Sodium salicylate	33,3	Limonene	
Thyme oil	31,77	Eucalyptol	
		Safrol	
		Potassium sulphocyanide	

We cannot here go into the experimental details of Geinitz' work, and we must content ourselves therefore with the reproduction of two tables, one showing the results of narcotising experiments with fish, and the other those of antiseptic experiments with milk. In both cases the experiments have been graded according to the degree of efficacy of action.

The paper further contains a description of the experiments for ascertaining the action of Δ^1 -*p*-menthenone-3 which have already been published as a supplement to our *Bericht* of April 1911.

In conclusion, Geinitz describes certain experiments in ascertaining the action of umbellulone, to which we referred in our *Report* of April 1909 (p. 116) in connection with an investigation by Prof. Kobert. It was found that even in a dilution of 1:15 000 (by weight) umbellulone exercised a powerful narcotic action upon fish. For purposes of comparison experiments were made with alcohol and ether, from which it appeared that to narcotise deeply a healthy specimen of fish, 20 cc. ether or alcohol to 3 litres water is required, which represents a concentration by weight of 1:166 and 1:190 respectively. The result of respiration-experiments with frogs showed that 1 drop (= 0,045 g.) umbellulone sufficed to produce a complete and extraordinarily deep narcosis. Experiments with rabbits also showed that, when injected hypodermically, umbellulone is capable of exercising narcotic action upon these animals, but that that action is accompanied by dangerous collateral effects, as already stated in our *Report* of April 1909 (p. 116).

The greater part of the essential oils and their derivatives used in the experiments had been placed by us at the author's disposal.

A detailed publication on the behaviour of the alicyclic compounds which occur in combination of glucuronic acid in the organism has appeared from the pen of J. Hämäläinen¹⁾, to whose work we have already referred several times²⁾. The substances in question, in olive oil solution and in the proportion of 1:5 to 10, according to their degree of solubility, were administered once daily to rabbits by means of a stomach-tube, the daily dose varying according to its toxicity, from 0,5 to 2,5 grams. The substances thus administered were found again in the urine, usually in combination with glucuronic acid. In the course of the investigation it was shown that the hydrocarbons are hydroxylised, at least in part, by simple oxidation, and that probably only secondary alcohols are formed in this process. In the case of the unsaturated hydrocarbons menthene, sabinene, pinene, and nopinene the double bond is not attacked, the combined acids which are formed being unsaturated. Menthene is converted into menthenol-2 or -6; sabinene into sabinenol-3 or -5; pinene perhaps into pinenol-3, and nopinene possibly into nopinenol-2 or -3. Saturated camphane deviates in its behaviour to this extent that it is converted into borneol, and not into β -borneol³⁾, for, as a rule, the oxidation *in vitro* does not occur side by side with the methyl-group.

The primary alcohols combine without change. The secondary alcohols dihydrocarveol, thujyl alcohol, sabinol, α -santenol, fenchyl- or isofenchyl

¹⁾ *Skand. Arch. f. Physiologie* 27 (1912), 141. From a reprint kindly sent to us.

²⁾ *Report* April 1909, 113; April 1911, 157.

³⁾ *Comp.* p. 159.

alcohol, and camphenilol, the tertiary alcohols β -santenol and camphene hydrate and the divalent terpin yield corresponding combined glucuronic acids. But as a result of secondary processes other bodies may be generated, as for instance in the case of thujyl alcohol, which is converted by hydration into *p*-menthane-diol-2,4. With sabinol, also, hydration is not improbable.

The behaviour of camphenilone is interesting. It is hydroxylised by reduction and in this reaction behaves like the aliphatic ketones, whereas the other terpene ketones which have so far been tested are either oxidised or, like thujone, undergo great alteration. Camphenilone is eliminated in the form of camphenilol glucuronic acid; menthone is probably oxidised into the tertiary ketonic alcohol 4-hydroxymenthone, thujone yields *p*-menthane-2-one-4-ol-glucuronic acid, and santenol gives rise to the keto alcohol santenonol.

Highly interesting are the observations of Hämäläinen on the behaviour of racemic bodies in the organism. In contradistinction to camphor and borneol, the *d*-component of camphenilone, camphenilol and santenone combines with glucuronic acid to a greater extent, than does the corresponding optical antipode.

A considerable number of the substances tested by Hämäläinen have been placed at his disposal by our firm.

As demonstrated by experiments on cats, dogs, and rabbits¹⁾, the first effect of the introduction of camphor into the animal circulation is to inflate the pulmonary cells, followed by an inflation of the cells of the whole circulatory system. This results in a diminution of the pressure in the right valve of the heart. These processes may acquire special importance when the respiratory course within the lungs is somewhat narrowed and the blood-pressure has been reduced. This explains the favourable action of the continued camphor-treatment in pulmonary tuberculosis.

The toxicity of turpentine oil is dealt with on p. 110.

On the pharmacological action of cineol see p. 120.

Phyto-physiological Notes.

In our *Report* of April 1911, p. 160, we referred to the interesting publication by Curtius and Franzen on the occurrence of α,β -hexylenic aldehyde in the leaves of certain plants. Since that time a detailed paper

¹⁾ E. Liebmann, *Arch. f. exp. Pathol. u. Pharmac.* 68 (1912), 59. Quoted from *Chem. Zentralbl.* 1912, II. 46.

on this subject has been published¹⁾ which enables us to complete our previous statements. For the purpose of preparing the aldehyde from 15 to 20 kilos green hornbeam leaves are ground up finely. The paste mixed with its own volume of water is distilled with steam, the total quantity of distillate recovered being 7 litres. The distillate is then diluted with an alcoholic solution of 7 grams *m*-nitrobenzohydrazide, which must have been previously freed from *m*-nitrodibenzohydrazide by recrystallisation from alcohol. As we have already stated in our previous abstract, the hexylenic-aldehyde-*m*-nitrobenzohydrazide obtained by this method has m. p. 166 to 167°, which is also the m. p. of the product prepared from the pure aldehyde. The *p*-nitrophenylhydrazone melts at 137°.

The m. p. of hexylenic aldehyde benzohydrazone lies between 112 and 113° (recrystallised from a mixture of benzene and ligroin). The aldehyde is recoverable from the hydrazone by boiling with dilute sulphuric acid. It boils at 47 to 48° (17 mm.) but apparently it cannot be distilled without showing indications of decomposition or polymerisation. It constitutes a colourless oil with a peculiar characteristic odour: $d_{40}^{17.9^{\circ}}$ 0,8470, $n_{D17.9^{\circ}}$ 1,44602. The α,β -hexylenic aldehyde was oxidised by Delépine's method, 2,2 g. of the aldehyde being dissolved in 50 cc. alcohol and diluted with a solution of 6 g. silver nitrate in 30 cc. water. A solution (say, seminormal) of 2,2 g. sodium hydroxide is next added to the mixture, slowly and under constant stirring, in the course of an hour, and finally the mixture is shaken up in the machine for 3 hours. The α,β -hexylenic acid separates out from the liquid which has been filtered off from the silver; it is oily at first, but when cooled with ice it immediately congeals into a colourless crystalline mass. After purification from light petroleum it has m. p. 32 to 33°. By the addition of bromine it yields α,β -dibromo caproic acid (m. p. 71 to 72°).

The presence of hexylenic aldehyde in the following plants was demonstrated: Grape vine (*Vitis vinifera*), edible chestnut (*Castanea vesca*), common oak (*Quercus sessiliflora*), brake, elder (*Sambucus racemosa*), common hazel (*Corylus avellana*), horse chestnut (*Aesculus Hippocastanum*), birch (*Betula alba*), common beech (*Fagus sylvatica*), clover (*Trifolium repens*), raspberry (*Rubus Idæus*), willow, walnut (*Juglans regia*), Norway maple (*Acer platanoides*), poplar, acacia (*Robinia Pseudacacia*) and ash.

The precipitates which have been obtained with *m*-nitrobenzohydrazide by Reinke and Braumüller²⁾ from the distillates of certain other plants likewise, in some cases, consist chiefly of condensation-products of α,β -hexylenic aldehyde. Hence the following plants should be added to those which have been examined by Curtius and Franzen: *Syringa vulgaris*, *Ægopodium Podagraria*, *Polygonum sachalinense*, *Ulmus campestris*, *Sambucus nigra*, *Alnus incana*, and *Vinca minor*.

¹⁾ Curtius and Franzen, *Liebigs Annalen* 390 (1912), 89.

²⁾ Comp. Report April 1911, 160.

In none of the plants examined by them, Curtius and Franzen failed to find the aldehyde, and it is therefore permissible to assert with reasonable confidence that it occurs in all green plants.

Its occurrence is closely allied with the assimilation of carbonic acid, for Reinke and Krätschmar have shown that the distillates of plants which had been kept in the dark for some days no longer possessed any power of reduction, whereas that power returned as soon as they were again exposed to light. The aldehyde is probably an intermediary product in the formation of other bodies which are essential to plant-life.

All the possible reduction-products of α, β -hexylenic aldehyde have been shown to exist in the vegetable kingdom. A hexylene alcohol, probably α, β -hexylene alcohol, has been discovered by van Romburgh¹⁾ in tea oil. This hexylene alcohol is readily convertible into hexylic aldehyde (caproic aldehyde) by migration of the double bond. We have shown²⁾ that it is probable that the same alcohol occurs in oil of *Eucalyptus Globulus*. Further reduction of the caproic aldehyde results in hexyl alcohol which, in the esterified form, occurs in certain essential oils.

It is impossible for us here to enter into details of the exceedingly noteworthy observations by the authors in the possible conversions of the aldehyde into carbohydrates. For these details we must refer to the original paper.

In order to obtain a knowledge of the volatile acids which exist in hornbeam leaves, Curtius and Franzen³⁾ subjected the finely ground leaves to steam-distillation and added to the distillate cold saturated baryta-water until it gave a faintly alkaline reaction. The whole mixture was then distilled by steam, the volatile acids thus being left behind in the distillation residue in the form of baryta-salts. The solution of the baryta salts was further evaporated *in vacuo*, diluted with phosphoric acid, and treated with steam until the distillate ceased to give an acid reaction. The distillate was then extracted with ether and the aqueous and ethereal solutions were worked up separately. The aqueous solution was found to contain formic and acetic acids. The ethereal extract contained traces of a hexylenic acid which, however, was not the acid corresponding to α, β -hexylenic aldehyde, but was probably identical with the acid $C_6H_{10}O_2$ which has been prepared from croton oil by Schmidt and Berendes⁴⁾. It is probable that hornbeam leaves also contain one or more homologues of this acid.

The liquid which had been distilled off from the baryta salts of the acids had a pronounced odour of α, β -hexylenic aldehyde. With the object

¹⁾ Report of the Botanical Gardens at Buitenzorg, 1895, 119. Also see Report April 1897, 40.

²⁾ Schimmel's Bericht April 1888, 18.

³⁾ Sitzungsberichte der Heidelberger Akademie der Wissenschaften. Sect. B, 1st paper. From a copy kindly sent to us.

⁴⁾ Liebigs Annalen 191 (1878), 121.

of oxidising the aldehydes it was vigorously stirred for about 3 hours with freshly precipitated silver oxide. When the odour of α,β -hexylenic aldehyde has disappeared the oxidation-process is at an end. By treating the mixture with baryta solution the silver salts were converted into the baryta salts. The whole mass was filtered and a certain portion of the distillate was distilled off, after which the remainder passed over without giving any odour. The acids corresponding to the aldehydes are then found to be contained in the distillation residue in the form of baryta salts.

Part of the baryta salts was used for the identification of the formic acid¹⁾. It was identified by the behaviour of its silver salt (turning black when heated), by the reduction of the mercuric chloride, and, lastly by its behaviour towards concentrated sulphuric acid (formation of carbonic oxide). These tests proved the presence of formaldehyde in hornbeam leaves. It is not possible to detect the aldehyde in the plants by the aid of colour-reactions, but by the method described above it can be identified above suspicion. It occurs in the leaves in exceedingly small proportions only.

With the object of demonstrating the presence of the other acids corresponding to the aldehydes, Curtius and Franzen²⁾ distilled the baryta salts with phosphoric acid. The distillate was extracted with ether and the ethereal and aqueous portions were worked up separately. In the portion soluble in water the formic acid was destroyed by heating with an excess of yellow mercuric oxide on the water-bath. The authors attempted to separate the remaining acids by fractional precipitation with silver nitrate, but without success. Ultimately the separation was effected by fractional distillation. The presence in the aqueous solution of acetic and butyric acids was established; propionic acid was either absent or occurred in traces only.

The acids which were present in the ethereal solutions were also separable by fractional distillation. The following were found present: *n*-butyric acid, α,β -hexylenic acid, and most probably valeric acid. It follows that hornbeam leaves contain formaldehyde, acetaldehyde, *n*-butylic aldehyde, α,β -hexylenic aldehyde and several of the higher homologues of hexylenic aldehyde. By far the principal of these, in respect of quantity, is hexylenic aldehyde; acetaldehyde and *n*-butylic aldehyde also occur in considerable proportions, but the others are only slightly represented.

For the purpose of identifying propionic acid the authors attempted to convert it into its hydrazide, but when heating with anhydrous hydrazine they obtained an already known body, namely diethyl-*n*-amido-triazol, m. p. 166 to 167°.

¹⁾ Curtius and Franzen, *Sitzungsberichte der Heidelberger Akademie der Wissenschaften*. Section A, 7th paper. This paper, as well as Nos. 8 and 9 have been kindly sent to us by the authors.

²⁾ *Ibidem*, 8th paper.

Upon oxidising the solution containing the aldehydes with oxide of silver the alcohols had remained unattacked; they were removed from the reaction-mass by steam distillation. When carefully tested¹⁾ the alcohol mixture was found to consist of butylene alcohol, pentylene alcohol, hexylene alcohol, an alcohol $C_8H_{14}O$ and several of the higher alcohols. It is not yet certain, although it is probable, that the hexylene alcohol which is found in hornbeam leaves is identical with that which was discovered by van Romburgh²⁾ in tea oil.

A treatise by Nellie Wakeman, which has been published as a *Bulletin* of the University of Wisconsin, No. 448, Science Series, Vol. 4, No. 4, contains a review of the phyto-chemical work relating to the various *Monarda*-species (N. O. Labiatae³⁾). It is not necessary for us to refer in detail to this publication, seeing that everything which concerns our special domain has already been discussed in our *Reports* under the heading of the particular oils. Botanically, the *Monarda*-genus appears to have been very little investigated. The known species, numbering about 26, together with their 36 synonyms, have been brought together in table-form by the authoress.

A few *Monarda*-species have been examined for their oxidase content, in the course of which investigation it was found that the young upper leaves contain the largest proportion of these ferments.

H. Hérissé⁴⁾ has isolated from the leaves of *Photinia serrulata* Lindl. (N. O. Rosaceae), the familiar amygdonitrile glucoside which splits off hydrocyanic acid.

It had already previously been discovered that *Photinia serrulata* belongs to the group of plants which yield hydrocyanic acid⁵⁾.

An article by E. Bourquelot and M. Bridel⁶⁾ deals with the synthetising action of emulsin. The authors found that a mixture of anhydrous glucose, saligenin, and emulsin in 85 p. c. alcohol gives rise to an amorphous, transparent body readily soluble in water; $[\alpha]_D - 30,02^\circ$. This compound is identical with the β -ethylglucoside of Königs and Knorr⁷⁾.

The β -methyl- and the β -propyl glucosides⁸⁾ have also been obtained by Bourquelot and Bridel⁹⁾. They have further demonstrated by experiment

¹⁾ 9th paper.

²⁾ *Loc. cit.*

³⁾ *Comp. Report* Oktober 1904, 58.

⁴⁾ *Journ. de Pharm. et Chim.* VII. 5 (1912), 574; *Bull. Soc. chim.* IV. 11 (1912), 680.

⁵⁾ Gildemeister and Hoffmann, *Die ätherischen Öle*. 2nd ed., Vol. I, p. 550.

⁶⁾ *Journ. de Pharm. et Chim.* VII. 5 (1912), 569; 6 (1912), 13.

⁷⁾ *Berl. Berichte* 34 (1901), 957.

⁸⁾ *Ibidem* 56, 97.

⁹⁾ *Ibidem* 164.

that emulsin has both a synthetising and a hydrolysing action¹⁾. To prove this they diluted solutions of β -ethylglucoside and glucose in ethyl alcohol of different strengths with emulsin and after some lapse of time estimated the proportion of glucose which was present in the solutions. It was then shown that the synthetising action of emulsin increases with the concentration of the alcohol. For example: with 95 p. c. alcohol 90 p. c. of the glucose used had been converted into the glucoside after a lapse of 50 days. When 90 or 85 p. c. alcohol was used the reaction was accomplished sooner, but only 70 p. c. glucoside was formed.

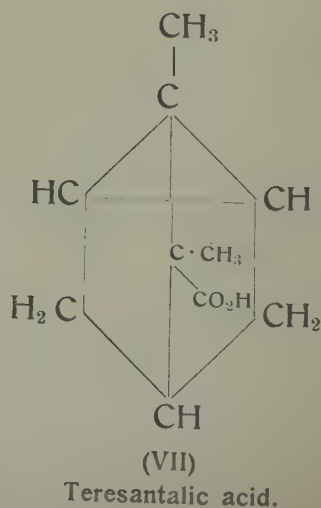
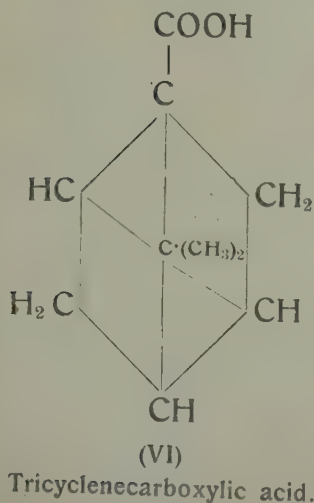
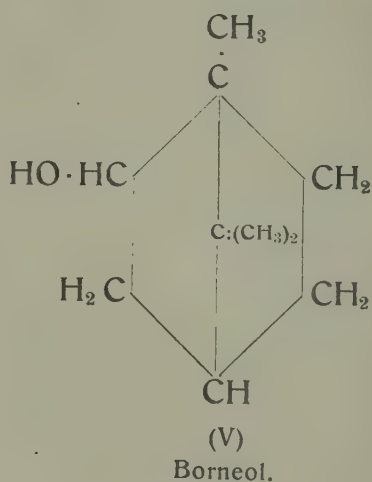
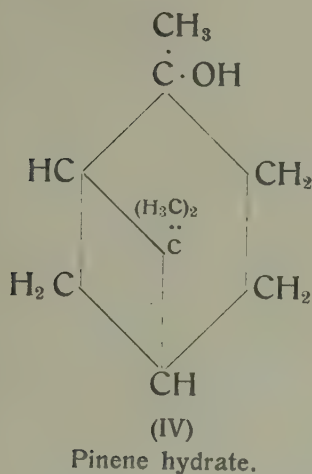
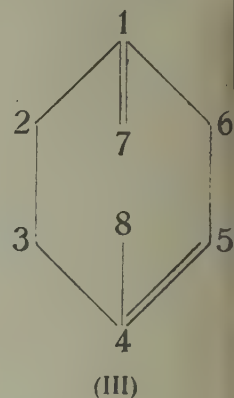
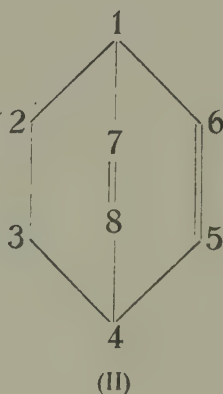
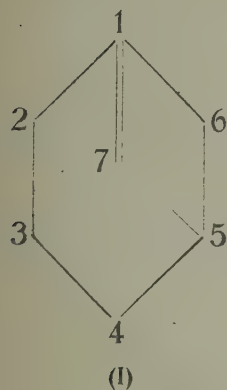
Chemical Notes.

V. Grignard²⁾ has proposed a new nomenclature for polycyclic hydro-aromatic systems. In his opinion his nomenclature is more lucidly arranged than that of von Baeyer. Grignard starts from a fundamental ring, which is crossed by one or more bridges. The system is not called by the total number of carbon atoms which it contains, but by the fundamental ring, the form of which is at once perceptible. The bridges are regarded as substitutes which are connected with the fundamental ring by their two terminal points and of which the position and nature are determined by the characteristic. In cases where only one bridge exists, the characteristic follows the prefix "*Bicyclo*". The characteristic consists seriatim of the figures of all the carbon-atoms which compose the bridge, including its connecting points. By this means it is at once clear from which point of the fundamental ring the bridge starts, where it ends, and what carbon atoms it contains. If the bridge consists of more than two carbon atoms the maximum value of the characteristics indicates at the same time the total number of cyclic carbon atoms which are present. A double linking in the bridge is indicated by the prefix "*Bicycleno*" in lieu of "*Bicyclo*". Thus, for example, according to Grignard the systems I, II and III are respectively called *bicycleno*-(1',7,5)-hexane, *bicycleno*-(1,7'8,4)-hexene-5 and *bicycleno*-(1',7,8,4)-hexene, while according to von Baeyer they are known as: *bicyclo*-(1,1,3)-heptene-1,7, *bicyclo*-(2,2,2)-octadiene-5,7 and *bicyclo*-(2,2,2)-octadiene-4(1,7). Grignard's principles are also readily applicable in those cases where the fundamental ring contains several bridges. The number of rings as indicated in the prefix is determined by doubling the number of the bridges. Pinene hydrate (IV) and borneol (V) would under Grignard's system be described as trimethyl-1,7,7-*bicyclo*-(2,7,4)-hexanol-1 and trimethyl-1,7,7-*bicyclo*-(1,7,4)-hexanol-2, while in Baeyer's system pinene hydrate is known as trimethyl-2,7,7-*bicyclo*-(1,1,3)-heptanol-2 and borneol as trimethyl-1,7,7-*bicyclo*-(1,2,2)-heptanol-2. In the new

¹⁾ Comp. Report April 1909, 17; October 1909, 19; October 1910, 18.

²⁾ Bull. Soc. chim. IV. 11 (1912), 124.

nomenclature, therefore, it is unnecessary to begin a fresh notation when the bridge-point changes from 2 to 1. Ring-systems with 2 bridges also for which up to the present no nomenclature existed, can readily be named by Grignard's system. For instance, tricyclene carboxylic acid (VI) and teresantalic acid (VII) can be described as dimethyl-1,7,7-tetracyclo- $\left[1,7,4\right]_{1,5}$ -hexane carboxylic acid-1 and dimethyl-1,7-tetracyclo- $\left[1,7,4\right]_{2,6}$ -hexane carboxylic acid-7 respectively.



In our *Report* of April 1912, p. 165, we mentioned a method devised by Klimont and Neumann for determining a standard for the unsaturated character of hydroaromatic compounds. G. O. Gaebel¹⁾ has tested by this method a series of bodies with double bonds and has found that peculiarities of a structural nature, such as the presence and position of highly negative radicals, the number of double bonds and steric conditions, certainly play an important part, for which reasons the method is often found wanting.

C. Harries²⁾, in a recently-published communication, has expressed the opinion that the so-called catalytic decomposition of ozone by soda liquor and concentrated sulphuric acid depends in the first place upon the destruction of oxozone (O_4). Harries, however, believed that the ordinary 12 to 14 p.c. ozone contained comparatively little oxozone and that liquefaction of the crude ozone was needed in order to accumulate the oxozone content. More recent investigations have shown this assumption to be incorrect, and Harries³⁾ now assumes that ordinary 11 to 14 p.c. ozone, as prepared in parallel connected Berthelot-tubes at a tension of about 8200 volts and a frequency of the alternating current of 100 second-periods, consists to the extent of about one-third of oxozone. He assumes this because soda liquor and concentrated sulphuric acid destroyed 4,7 p.c. out of 14 p.c. at 15 l-hours' velocity, and 6,2 p.c. out of 11 p.c. at 10 l-hours' velocity. If this observation is correct, it follows that it must be possible to obtain normal ozonides with washed ozone from all the compounds which, up to the present, have yielded upon ozonisation oxozonides or mixtures of O_3 - and O_4 -ozonides. As a matter of fact, when 4,8 to 9,3 p.c. ozone was passed through a solution of pinene in hexane, the ozonide $C_{10}H_{16}O_3$ was separated out in the form of a solid white mass. Terpeneol in hexane solution also yielded a solid, white, normal ozonide; from citronellal in hexane solution the normal ozonide separated out in the form of a colourless oil.

Hydrocarbons.

By passing linalool vapour over active copper at 130 to 140°, C. J. Enklaar⁴⁾ obtained a hydrocarbon $C_{10}H_{16}$, which is probably identical with myrcene: b. p. 62° (14 mm.), $d_{150} 0,802$, $n_{D150} 1,47$. The same hydrocarbon is generated when linalool is heated with phenyl isocyanate. Hydrogenation of the hydrocarbon with nickel and hydrogen at 130° yields 2,6-dimethyloctane.

¹⁾ *Arch. der Pharm.* 250 (1912), 72.

²⁾ *Zeitschr. f. Elektrochemie* 18 (1912), 130.

³⁾ *Berl. Berichte* 45 (1912), 936.

⁴⁾ *Chem. Weekblad* 9 (1912), 68. Quoted from *Chem. Zentralbl.* 1912, I. 726. Also compare *Report* October 1910, 187.

O. Wallach¹⁾ has already stated on a previous occasion that, under suitable conditions, the chlorine of nitrosochloride additive products of the unsaturated hydrocarbons may be exchanged for the acetic acid radical, and that it is possible to reduce the nitrosochlorides directly into saturated bases and ketones by treating them in glacial acetic acid solution with zinc dust. Wallach²⁾ has recently studied these reactions in some of the simplest possible cases. The nitrosochloride of ethylidene-*cyclohexane* (m. p. 132°), when warmed with sodium acetate in glacial acetic acid, yielded the oxime of acetyl-1-acetoxy-1-*cyclohexane* (m. p. 103°). This oxime was split up with 2 p. c. sulphuric acid, yielding tetrahydroacetophenone and a hydroxy ketone (m. p. of the semicarbazone 196°). The nitrosochloride of the ethylidenecyclohexane was converted by means of zinc dust in glacial acetic acid into hexahydroacetophenone (m. p. of the semicarbazone 176 to 177°). The acetic solution contained amidoethylcyclohexane. The nitrosochloride of methyl-1-ethylidene-3-*cyclohexane* yielded by the same method methyl-1-acetyl-3-*cyclohexane* (m. p. of the semicarbazone 180 to 181°).

Santene. I. Kondakow³⁾ has investigated the halogen hydrates of santene. In working on santene from oil of pine-needles he obtained both solid and liquid hydrochlorides. Santene from sandalwood oil (b. p. 139, to 140,5°) yielded additive products m. p. 55 to 59° (b. p. 65 to 66° at 8 mm) and m. p. 14 to 15° (b. p. 61 to 63° at 8 mm.). A compound, m. p. 66°, obtained from santene and hydrogen chloride gas, when treated with alcoholic potash liquor, was partly decomposed into a hydrocarbon (b. p. 138,5 to 142,5°). The residue was first resolved by means of concentrated potash liquor, when it yielded a hydrocarbon, m. p. 137,5 to 142°⁴⁾, as well as an ether. Santene from sandalwood oil, when treated in the cold with concentrated hydrobromic acid, yielded a solid product (m. p. 18 to 25°) and a liquid compound, m. p. 79 to 81° (8 mm). Both these bodies when treated with alcoholic potash liquor yielded santene (b. p. 139,5 to 142,5°) and an ether (b. p. 195°). Kondakow found santene acetate ($C_9H_{15}OCOCH_3$) to possess the following constants: b. p. 85 to 89 (8 mm.), $d_{20} 0,9859$, $n_D 1,45929$.

Bornylene. Bornylene, which owing to its extreme volatility cannot be recrystallised, is readily obtainable from bornyl xanthate. With the view of discovering whether bornylene prepared in this manner is uniform, L. Tschugaeff and W. Budrick⁵⁾ have oxidised with potassium per-

¹⁾ Comp. Report October 1910, 192.

²⁾ *Liebigs Annalen* 389 (1912), 188.

³⁾ *Journ. russ. phys. chem. Ges.* 43 (1911), 1107. Quoted from *Chem. Zentralbl.* 1912, I. 101.

⁴⁾ This should probably be b. p.

⁵⁾ *Liebigs Annalen* 388 (1912), 280.

manganate the hydrocarbon which they had recovered from the xanthate. In the course of this manipulation they obtained a yield of 70 to 73 p.c. camphoric acid. From the fraction which had not been attacked by the potassium permanganate they succeeded in isolating a hydrocarbon $C_{10}H_{16}$, m. p. 64,5 to 65; b. p. 153 to 153,5° ($[\alpha]_D - 8,34^\circ$) which is most probably identical with cyclene. The bornylene which was used for the purpose of oxidation possessed the following properties: m. p. 109 to 110° b. p. 146 to 146,5° (760 mm.), $[\alpha]_D + 19,30^\circ$ (in toluene solution). The resolution of the xanthate is best carried out at 176 to 177° by heating the product in a test-tube for about 24 hours in boiling limonene. The bornylene then condenses in the upper part of the tube and may easily be removed with a spatula. No racemisation takes place when the xanthate is decomposed.

The *d*-borneol employed in the preparation of *l*-bornylene had been placed by us at the author's disposal.

G. G. Henderson and W. Caw¹⁾ do not believe that the bornylene prepared from the xanthate by Tschugaeff is chemically pure, and suspect it to contain an isomeric terpene. The bornylene, however, which Bredt and Sandkuhl²⁾ prepared from camphor, from primarily-produced camphor-carboxylic acid, borneol-, bornylene-, and bromohydrobornylene carboxylic acid, they regard as absolutely pure. They also regard as chemically pure the hydrocarbon prepared by Bredt and Hilbing³⁾ from β -iodohydrobornylene carboxylic acid.

According to Henderson and Caw, a simple method of obtaining absolutely pure bornylene consists in treating the crude bornylene prepared from its xanthate with hydrogen peroxide in glacial acetic acid. For this purpose they dissolved 50 g. bornylene in 300 cc. glacial acetic acid and heated the mixture with 10 cc. of 30 p.c. aqueous hydrogen peroxide solution to from 60 to 65° until the subliming crystals gave m. p. 110 to 112°. After cooling, the bornylene which had separated out was pressed off, and the ethereal solution of the hydrocarbon dried with sodium. The bornylene purified by this method has m. p. 113°: $[\alpha]_{D_{200}} - 22,27^\circ$ (8,98 p. c. solution in benzene). As the crude material, *d*-borneol, contained a little *l*-borneol, the sp. rot. of the bornylene is rather too low.

The purifying action of the hydrogen peroxide appears to be due to the fact that the impurities are more readily attacked than is the bornylene itself.

On the preparation of nitrosopinene from pinocamphonoxime, see p. 166.

On pure α - and β -thujene, see p. 153.

¹⁾ *Journ. chem. Soc.* **101** (1912), 1416.

²⁾ *Liebigs Annalen* **366** (1909), 11; *Comp. Report* October **1909**, 195.

³⁾ *Journ. f. prakt. Chem.* **II. 64** (1911), 778; *Comp. Report* April **1912**, 191.

Methylpulegene. H. Rupe¹⁾, in collaboration with H. Schobel and E. Abegg, has continued his investigations into terpene homologues, to which we have already repeatedly referred²⁾. The attempts to obtain well-defined compounds by oxidising homomenthene with ozone in glacial acetic acid solution remained without result. The authors were more successful with the hydrocarbon methylpulegene, which is formed from pulegone and magnesium methyl halogenide. As oxidation-product the isolated, in addition to acetone, a keto acid, γ -methyl- δ -acetylvaleric acid (m. p. of the semicarbazone 150°) which, when oxidised with sodium hypobromite, yielded β -methyladipic acid, and with nitric acid α -methylglutaric acid. The formation of the keto acid does not permit of any definite conclusions as to the structure of the hydrocarbon.

In a few cases the authors have succeeded in preparing the tertiary alcohol methylpulegol from pulegone and magnesium ethyl bromide: b. p. 93 to 94 (10,5 mm.). In the process of preparing methylpulegene, methylmenthone (homomenthone) had been formed as a by-product: b. p. 93 (11 mm.), m. p. of the semicarbazone 186°.

Caryophyllene. In his fifth paper on the sesquiterpenes, E. Deussen³⁾ describes a few derivatives of, as well as a sensitive test for, caryophyllene. When β -caryophyllene nitrosite is heated with ligroin there results, in addition to dehydrocaryophyllene nitrosate, a body which is distinguished by its insolubility and which can be purified by dissolving it in acetone and precipitating with light petroleum. It crystallises in the pure state in white needles, m. p. 159°, and shows some points of resemblance to Harries' India rubber nitrosite⁴⁾. (Dec. p. 158 to 162°). The same body is generated when nitrous acid gas is passed into an ethereal solution of caryophyllene. A blue coloration quickly results, and when the passing-in of the gas is continued for some time a voluminous yellowish-white body is precipitated, while the blue colour disappears. Careful re-solution from acetone or hot acetic ester yields a body in the form of well-developed white, silky needles, dec. p. 159 to 160°. In contradistinction to previous statements, this body is optically active: $[\alpha_D] - 133^\circ 50'$ (1,037 p. c. solution in acetone). Combustion showed the structure to be $C_{12}H_{19}N_3O_6$. Owing to its insolubility in most of the organic solvents, this compound is excellently adapted for the detection and determination of β -caryophyllene. For this purpose from 2 to 3 g. of the oil-sample under examination is treated in a 10 p. c. ethereal solution with nitric oxides, the reaction-mixture (which should be protected from light) not being cooled, and the

¹⁾ *Berl. Berichte* 45 (1912), 1528.

²⁾ *Comp. Report* October 1906, 130; November 1908, 186; April 1912, 190.

³⁾ *Liebigs Annalen* 388 (1912), 136.

⁴⁾ *Ibidem* 383 (1911), 199.

passing-in of the reagent being discontinued as soon as separation ceases. After being washed out with ether the precipitate is weighed. By this method, Deussen discovered in Pará copaiba balsam oil 5,15 p. c. and in Maracaibo copaiba balsam oil 2 p. c. β -caryophyllene. The presence of the two caryophyllenes in copaiba balsam oil had already been observed by us some time previously¹⁾. In African copaiba balsam oil 0,87 p. c. β -caryophyllene was found present. The low-boiling portions of West Indian sandalwood oil also contained β -caryophyllene.

Deussen has also examined hop oil, in which distillate, in addition to α -caryophyllene (the presence of which he had already ascertained previously)²⁾, he determined the presence of small quantities of β -caryophyllene. On this occasion he also obtained a nitrosite of α -caryophyllene.

The author next refers to the caryophyllene which has been recovered from caryophyllene dihydrochloride by Semmler and Mayer³⁾. In his opinion it is doubtful whether this caryophyllene is a uniform body.

In the same paper Deussen discusses the detection of the two double bonds in α - and β -caryophyllene. Hydrogenation by Paal's method of a mixture of α - and β -caryophyllene yielded dihydrocaryophyllene (b. p. 129 to 130° at 14 mm.; d_{190} 0,8898; α_D — 25°; n_{D20} 1,49032). The author was not successful in reducing⁴⁾ the second double bond by hydrogen, although he was able to saturate it with hydrochloric acid, bromine &c. Deussen proved the existence of an ethylene-bond in α -caryophyllene nitrosite by brominating this body in a chloroform-solution, when 2 bromine atoms were absorbed, producing a hydrobromo-nitrosochloride, m. p. 144 to 145°. The fact that β -caryophyllene nitrosite contains yet another double bond is shown by the generation of β -hydrochloro-caryophyllene-nitrosite (m. p. 137°) when dry hydrochloric acid gas is passed into the ethereal solution of the β -nitrosite. This compound occurs in the form of deep blue needles. Its sp. rot. is extraordinarily high, viz., +930,4°. β -Caryophyllene nitrosite also possesses a very high rotation; the values +102,95 and +162,49°, given for this body by Kremers and by Deussen-Lewinsohn have been erroneously calculated, the correct figures being +1029,5 and +1626,0°. Deussen and Vielitz found $[\alpha_D]$ +1661,1° (0,1713% solution in ligroin).

According to Haarmann⁵⁾ the glycol-like compound $C_{15}H_{22}O_4$ which was obtained by Deussen when oxidising caryophyllene with potassium permanganate⁶⁾, has the structure $C_{14}H_{22}O_4$. Deussen has once again submitted this body to combustion with the result that he again found

¹⁾ Report October 1910, 185.

²⁾ Comp. Report October 1911, 55.

³⁾ Berl. Berichte 43 (1910), 3451. Report April 1911, 171.

⁴⁾ Comp. p. 150.

⁵⁾ Comp. Report October 1909, 177.

⁶⁾ Comp. Report April 1909, 124.

the structure to be $C_{15}H_{22}O_4$, or $C_{15}H_{24}O_4$. It appears to be a point of importance to carry on the process of combustion with extreme slowness.

Finally the author refers to the structure of the product of elimination of β -caryophyllene nitrosite with alcoholic potash-solution; he surmises that in this case the NO_2 -group is replaced by the ethoxy-group.

F. W. Semmler and E. W. Mayer¹⁾ have reduced natural caryophyllene in absolute ether by passing hydrogen into it, in the presence of platinum black. The resulting tetrahydrocaryophyllene constituted a liquid, b. p. 122 to 123° at 12 mm. ($d_{20} 0,8712$; $\alpha_{D20} + 3^\circ$; $n_{D20} 1,4700$) which was identical with the reduction product prepared from regenerated caryophyllene. From this it may be concluded that the same hydrocarbon-structure occurs both in natural and in regenerated caryophyllene.

Cedrene. Artificial cedrene, which is obtained by splitting off water from cedrol, has up to the present been regarded as an isomeride of natural cedrene. F. W. Semmler and K. E. Spornitz²⁾, by resolution of the artificial products, have shown this assumption to be inaccurate. They prepared the hydrocarbon by heating cedrol (m. p. 79 to 80°) during 15 minutes with its own weight of 100 p. c. formic acid. The constants were b. p. 112 to 113° (at 7 mm.) and $\alpha_D - 85^\circ$. When the hydrocarbon was oxidised with ozone in glacial acetic acid solution it gave rise to cedrene keto acid, which was identified by the preparation of its methyl ester (b. p. 166 to 168°; $d_{19} 1,0501$; $\alpha_D - 35^\circ$; $n_D 1,48482$). These constants agreed with those determined for the ketonic methylester from natural cedrene. Cedrene dicarboxylic acid also, prepared from artificial cedrene, proved to be identical with cedrene dicarboxylic acid from natural cedrene³⁾. The two preparations, when mixed together, gave no depression of m. p.

These experiments have proved that natural cedrene contains the artificial cedrene with a high rotation; it is probable that the natural product, owing to its b. p. being higher, contains still other isomeric sesquiterpenes; possibly a little semicyclic cedrene may be assumed in the form of an admixture.

Sterene. A new manner of representing the hydrocarbons of the styrene-series is described by F. Kunckel⁴⁾. This author has discovered that the propenyl hydrocarbons may readily be prepared from the α - β -dihalogen hydrocarbons by treating an ethereal solution of the latter, to which if necessary a small quantity of alcohol was added, with metallic sodium.

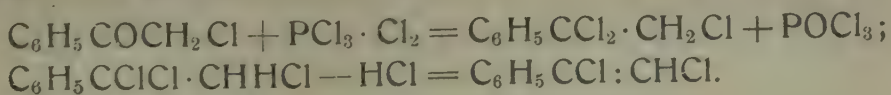
¹⁾ *Berl. Berichte* 45 (1912), 1393.

²⁾ *Berl. Berichte* 45 (1912), 1553.

³⁾ *Comp. Report* April 1912, 173.

⁴⁾ *Berichte d. deutsch. pharm. Ges.* 22 (1912), 180 242

Kunckel obtained the α - β -dihalogen products from the α -halogen ketones by reacting with phosphorus pentachloride after the following equation:



The hydrogen chloride was split off by distilling the trihalogen compounds which were formed as an intermediary product.

By the method above indicated the author obtained: propenyl benzene (b. p. 167 to 170°), 1-methyl-4-propenylbenzene, 1-*isopropyl*-4-propenylbenzene, 1-methyl-4-*isopropyl*-3-propenylbenzene; also *p*-propenyl-*o* and *m*-xylene and *o*-propenyl-*p*-xylene, as well as a few derivatives of *n*-butenylbenzene, namely: 1-methyl-4-butenylbenzene, 1,2- and 1,3-dimethyl-4-*n*-butenylbenzene, 1-*isopropyl*-4-butenylbenzene and 3-butenylcymene.

On the production of hydrocarbons from hydrazine compounds by boiling with solid potassium hydroxide, see p. 165.

Alcohols.

Some time ago Sabatier and Senderens¹⁾ reported on a simple method for the identification of alcohols, based upon the catalytic reaction of reduced copper at a temperature of 300° upon the vapours of the alcohols in question. The body under examination is converted into an aldehyde, a ketone, or a hydrocarbon, according to whether it is a primary, secondary, or tertiary alcohol. G. B. Neave²⁾ has shown that the terpene alcohols are attacked in a similar manner. He passed the vapours of *d*-borneol ($\alpha_{\text{D}_{20}} + 37,70^\circ$) over copper heated to 300°, with the result that he obtained *l*-camphor (m. p. of the oxime 159 to 161°). Menthol gave rise to menthone (m. p. of the semicarbazone 183 to 184°), terpeneol and terpin hydrate yielded dipentene (m. p. of the tetrabromide 122 to 124°), *isoborneol* a small proportion of camphene, together with a considerable proportion of unattacked alcohol, and *sobrerol* (pinolhydrate), pinol.

On a hydrocarbon obtained from linalol by heating with phenylisocyanate, see p. 145.

Menthol. According to a communication by J. B. Senderens³⁾, when menthol is distilled with 1 or 2 p. c. concentrated sulphuric acid, it yields menthene, b. p. 165 to 168°. Menthene is likewise formed by heating menthol with 4 to 5 p. c. dilute sulphuric acid (1:2). From this it follows that dehydration by dilute sulphuric acid is due to catalytic action, and not

¹⁾ *Bull. Soc. Chim.* III. 33 (1905), 263. Report October 1905, 100.

²⁾ *Journ. chem. Soc.* 101 (1912), 513.

³⁾ *Compt. rend.* 154 (1912), 1170.

to an abstraction of water, as would be supposed from the reaction with concentrated sulphuric acid. When treated with potassium bisulphate or boric acid menthol also splits off water. But the catalytic action of these reagents is considerably weaker than that of sulphuric acid.

H. Rupe and W. Kerkovius¹⁾ have demonstrated the possibility of complete steric decomposition of an inactive acid by means of menthol esterification. By allowing the chloride of α -phenylhydrocinnamic acid to react with menthol in the presence of pyridine they obtained two esters: one readily soluble, m. p. 58 to 62° ($[\alpha]_{D20} - 84,99^\circ$) and the other a high boiling, sparingly soluble body, m. p. 100 to 101° ($[\alpha]_{D20} - 21,97^\circ$). The esters obtained from the optically active acids by means of primarily produced strychnine salts give almost the same rotation values as do the esters mentioned above, namely, $[\alpha]_{D20} - 89,06^\circ$ and $[\alpha]_{D20} - 21,97^\circ$. It is a peculiar fact that the two optically active α -phenylhydrocinnamic acids were rendered completely inactive after a short time by alcoholic potash.

Thujylalcohol. The paper on thujylalcohol published by Paolini in the *Rendiconti della R. Accad. dei Lincei* (Vol. 20, I. Part. 10, p. 765)²⁾ has lately been published in the *Gazzetta chimica ital.* 42 (1912), I. 41³⁾.

V. Paolini and B. Divizia⁴⁾ call attention to the differences in the constants which have been observed for thujyl alcohol. They quote a compendious bibliography, and set forth a table of the constants of thujyl alcohols prepared by different methods.

The method described by Paolini⁵⁾, namely the purification of the acid phthalic ester by repeated recrystallisation is, according to L. Tschugaef and W. Fomin⁶⁾, extremely cumbersome. A simpler method consists in first recrystallising the cinchonine salt of the ester 3 or 4 times from alcohol, and finally isolating the pure alcohol by hydrolysing with potash liquor and driving off with steam. By this method the authors obtained from the acid phthalate of crude thujyl alcohol, *d*-thujyl alcohol ($[\alpha]_D + 116,93^\circ$) of the density $d_{40}^{20} 0,9187$. The mother liquors remaining after the separation of the crystalline cinchonine salt were worked up for free phthalic ester, which can be most readily purified from the primarily produced strychnine salt, which is sparingly soluble. The regenerated

¹⁾ *Berl. Berichte* 45 (1912), 1398.

²⁾ *Comp. Report* October 1911, 142.

³⁾ *Chem. Zentralbl.* 1912, I. 1011.

⁴⁾ *Atti R. Accad. dei Lincei*, Roma (5), 21, I. 570. Quoted from *Chem. Zentralbl.* 1912, II. 256. The authors have very kindly sent us a reprint of their paper.

⁵⁾ *Comp. Report* October 1911, 142.

⁶⁾ *Berl. Berichte* 45 (1912), 1293.

l-thujyl alcohol gave $[\alpha]_{D_{20}} - 9,12^\circ$ and was solid at ordinary temperature: m. p. 28° . The liquid *d*-thujyl alcohol forms a xanthate which splits up at 138° ; the xanthate of the solid *l*-thujyl alcohol is more stable: decomp. pt. 183° . The xanthate of *d*-thujyl alcohol yields a hydrocarbon possessing the following constants: b. p. 151° (759 mm.), $d_{40}^{20} 0,8301$, $n_{D_{20}} 1,45150$. Most probably this body represents pure α -thujene. The decomposition of *l*-thujylxanthate leads in all probability to β -thujene (b. p. 147° at 739 mm.).

Guajol. In order to discover a solution of the question how many ring-systems and double-bonds occur in guajol, F. W. Semmler and E. W. Mayer¹⁾ calculated the molecular refraction of the alcohol in question from its sp. gr. and its index of refraction, and calculated both the refractive index and the specific gravity for a temperature of 20° . The values ascertained for guajol as well as for several other sesquiterpene alcohols are set forth in table-form below. It follows from these that guajol is a bicyclic alcohol with a double bond. For purposes of identification it is oxidised with potassium permanganate in aqueous acetone, giving rise to a glycerol $C_{15}H_{24}O_3$, m. p. 210 to 211° , which body is possibly the first glycerol of the sesquiterpene series. Ozonisation in glacial acetic acid solution yielded a neutral decomposition product, [b. p. 138 to 144° (7 mm.) $d_{20}^{20} 0,9972$; $\alpha_{D_{20}} + 96^\circ$; $n_D 1,5276$], possibly an oxide. Besides this, there was formed a body $C_{15}H_{24}O_3$, apparently a keto lactone: b. p. 200 to 208° (8 mm.), $d_{20}^{20} 1,067$, $n_{D_{20}} 1,5005$.

		d_{40}^{20}		$n_{D_{20}}$		Mol.-Refr.	
						found	calc.
Guajol	d_{20}^{20}	0,9074	0,9714	$n_{D_{100}} 1,4716$	1,5100	68,35	68,07
Ledum camphor . . .	d_{20}^{20}	0,9094	0,9814	$n_{D_{110}} 1,4667$	1,5072	67,35	6,078
Eudesmol	d_{20}^{20}	0,9209	0,9884	$n_{D_{90}} 1,4830$	1,5164	67,99	68,07
Solid Cedrol	d_{20}^{20}	0,9496	1,0056	$n_{D_{90}} 1,4824$	1,5139	66,46	66,36
Patchouly alcohol . .	d_{20}^{20}	0,9924	1,0284	$n_{D_{30}} 1,5029$	1,5245	66,19	66,36
Caryophyllene hydrate	d_{20}^{20}	0,9376	1,0016	$n_{D_{100}} 1,4755$	1,5155	66,90	66,36

bicyclic
tricyclic

sec.-Phenylethyl alcohol. B. Holmberg²⁾ describes the previously unknown optically active methylphenylcarbinols (secondary phenylethyl-alcohols). He started from the active phenyl ethylamines which, in dilute sulphuric acid solution, he treated under strong cooling with nitrous acid. *l*-Phenylethylamine gave rise to *d*-phenylethyl nitrite and to sec. *d*-phenyl-

¹⁾ Berl. Berichte 45 (1912), 1390.

²⁾ Berl. Berichte 45 (1912), 997.

ethyl alcohol. The nitrite forms an unstable golden-yellow oil with peculiar odour, reminding somewhat of turpentine: b.p. 72,5 to 73° (19 mm.) d_{40}^{20} 1,045, $\alpha_{D170} + 6,80^\circ$. Holmberg has not yet discovered a suitable method for preparing from the nitrite the corresponding alcohol. *d*-Phenylethyl alcohol had been produced in somewhat larger quantity. Its constants are given as follow: b.p. 98,5 to 99° (20 mm.), d_{40}^{20} 1,018, $\alpha_{D150} + 5,00^\circ$. In the experiment for preparing *l*-phenylethylalcohol from *d*-phenylethylamine the cooling-process had not been carried out sufficiently thoroughly, with the result that the alcohol generated only gave $\alpha_{D170} - 4,40^\circ$. It is therefore certain that when phenylethyl alcohol is formed, racemisation takes place, in proportion as the reaction temperature is higher. Conversion of the *d*-phenylethyl alcohol into the bromide by saturating it with hydrobromic acid gave rise to inactive α -bromomethylbenzene. *l*-Phenylethyl alcohol and phosphorus pentabromide led to a bromide with a fair dextrorotation: $\alpha_{D140} + 1,50^\circ$. The action of silver oxide upon the alcoholic solution of α -bromoethylbenzene resulted in the ethylether of phenylethyl alcohol, a colourless oil with an agreeable odour (d_{40}^{20} 0,928).

Cinnamic alcohol. As the crude material for an investigation into the transposition of ethylene linkings, H. Beaufour¹⁾ employed the methyl ether of cinnamic alcohol, the preparation of which he describes as follows: 40 grams sodium amide, reduced to fine powder under benzene ether, is gradually diluted in a flask with a solution of 150 grams cinnamic alcohol in 200 cc. benzene. In the course of about half an hour the alcoholate has been precipitated in the form of a solid mass. After this 150 grams methyl iodide is gradually added, and part of the sodium iodide which has separated out is drawn off. The cinnamyl methylether boils at 227° (117° at 16 mm.): d_{40}^{20} 1,0037. The ethylether obtained by the same method possesses the following constants: b.p. 127 to 129° (17 mm.) d_{40}^{20} 0,9938.

Aldehydes.

H. D. Law²⁾ has reduced by the electrolytical method a series of aliphatic and aromatic ketones and aldehydes. Generally speaking, the electrolytical reduction proceeds on the same lines as that with sodium amalgam, but it has the disadvantage that it does not permit work to be carried on at high temperatures. Methylheptenone was reduced very slowly in alkaline solution, but much more rapidly in sulphuric acid with lead cathodes. The reaction-products detected were methylheptenol, an isomeric oxide $C_8H_{16}O$, b.p. 127 to 129°, which has already been obtained by Wallach³⁾

¹⁾ *Bull. Soc. chim.* IV. **11** (1912), 648.

²⁾ *Journ. chem. Soc.* **101** (1912), 1016.

³⁾ *Liebigs Annalen* **275** (1893), 171.

on treating methylheptenol with dilute sulphuric acid, and, probably, an unsaturated hydrocarbon. Attempts at reducing citronellal remained without result. With citral, Law was more successful. This aldehyde afforded a mixture of geraniol with an unstable isomeric alcohol, b.p. about 220° , as well as a non-volatile compound $C_{20}H_{34}O_2$, which is perhaps identical with the pinacone-like compound prepared by Verley¹⁾. Menthone yielded a mixture of menthol and two isomeric menthopinacones. As a reduction-product of *d*-carvone ($\alpha_{D_{18}^{\circ}} + 61^{\circ} 35'$), Law obtained a body with b. p. between 260 and 262° (40 mm.), as well as α -carvelone (m. p. of the oxime 228°) and an as yet unknown isomeric carvelone, of which the oxime melted at 228° . Reduction of pulegone in alkaline solution gave rise to menthone, pulegopinacone (m. p. 119°), and menthopinacone (m. p. 148°); using sulphuric acid as a cathode liquid the result was menthol, menthone, and pulego- and menthopinacone. Cinnamic aldehyde resinified both in acid and in alkaline solution; in a solution of potassium acetate it yielded β -phenylpropylalcohol.

P. Sabatier and A. Mailhe²⁾ describe an interesting method of preparing aldehydes. Over titanium oxide heated to 250 to 300° they pass the vapours of a fatty acid mixed with an excess of formic acid vapour. From the fatty acid the corresponding aldehyde is produced, carbon-monoxide and -dioxide being liberated. Acetic acid yielded 50 p. c., propionic acid 40 p. c., butyric acid 55 p. c., isobutyric acid 65 p. c., isovaleric acid 75 p. c., isobutylacetic acid 80 p. c., caprylic acid 90 p. c. and pelargonic acid 85 p. c. of the corresponding aldehyde. It is not easy, by this method, to convert benzoic acid into benzaldehyde; phenylacetic acid yields 75 p. c. phenylacetaldehyde:

Ketones.

On the electrolytical reduction of ketones see above.

On the production of α -ionane from ionone, see p. 166.

O. Wallach³⁾ has found that the two ketones *cyclopentene*-pentanone and *dicyclopentene*-pentanone are capable of easy reduction by Paal's method, into the saturated ketones $C_{10}H_{18}O$ and $C_{15}H_{26}O$. In the course of this conversion *cyclopentene*-pentanone forms *cyclopentyl cyclopentanone* (b.p. 232 to 233° ; $d_{21}^{\circ} 0,9745$) a body with a pronounced odour of menthone. In an analogous manner as has been proved to be the case with *cyclohexylhexanone*⁴⁾, *cyclopentylpentanone* splits up during oxidation with chromic acid into a

¹⁾ Bull. Soc. chim. III. 21 (1899), 409.

²⁾ Compt. rend. 154 (1912), 561.

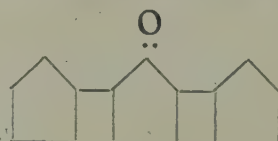
³⁾ Liebigs Annalen 389 (1912), 178.

⁴⁾ Comp. Report October 1911, 146.

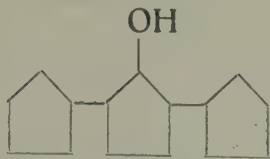
keto acid, δ -cyclopentyl- δ -keto-*n*-valeric acid (m. p. of the semicarbazone 181 to 183°). Reduction of cyclopentylpentanone in alcoholic solution with sodium gives rise to cyclopentylpentanol $C_5H_9 \cdot C_5H_8OH$, a liquid with b. p. 235 to 236°: $d_{170} 0,9785$, $n_{D170} 1,4884$, m. p. of the phenylurethane 88 to 89°. If cyclopentylpentanol is heated for about an hour to 150° with twice its own quantity of zinc chloride the result is a terpene, cyclopentylpentene (I), possessing the following constants: b. p. 196,5 to 198° $d_{19,50} 0,9080$, $n_{D19,50} 1,4938$, mol. refr. calc. for $C_{10}H_{16} \bar{=} 43,53$, found 43,59. This terpene, which contains two pentacyclic systems in simple bond with each other, is distinguished from the well-known bicyclic terpenes by its considerably higher b. p. Its nitrosochloride has m. p. 113 to 114°. Dicyclopentene-pentanone, which is formed to the extent of from 12 to 13 p. c. in the process of auto-condensation of cyclopentanone, when reduced by Paal's method readily absorbs four hydrogen atoms and is converted into saturated, colourless, dicyclopentylpentanone (II): b. p. 165 to 170° (12 mm.), $d_{190} 0,9925$. Oxidation of this ketone with chromic acid gives rise to a keto acid, α - δ -dicyclopentyl- δ -keto-*n*-valeric acid. Reduction of dicyclopentylpentanone with sodium and alcohol yields dicyclopentylpentanol (III) (m. p. 68°; b. p. 210° at 100 mm.) from which, when heated with zinc chloride to 150 to 200°, dicyclopentylcyclopentene (IV) is generated. This hydrocarbon possesses the structure of a sesquiterpene. It cannot be volatilised under ordinary pressure without decomposition: b. p. about 290°, 210° (100 mm.), $d_{200} 0,939$, $n_{D200} 1,5065$, mol. refr. found 64,40, calc. for $C_{15}H_{24} \bar{=} 64,45$.



Cyclopentylpentene (I).



Dicyclopentylpentanone (II).



Dicyclopentylpentanol (III).



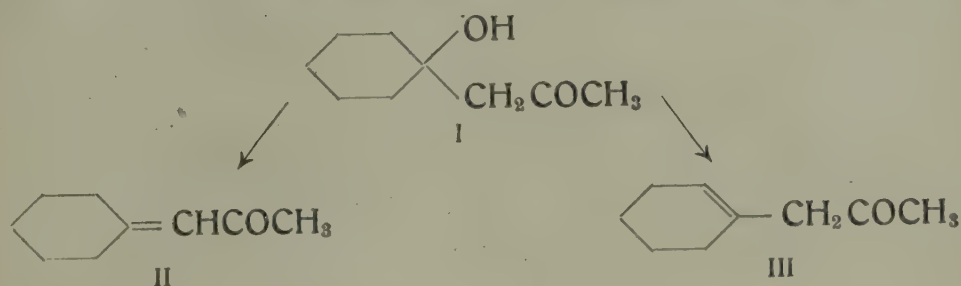
Dicyclopentylcyclopentene (IV).

Many years ago Wallach¹⁾ showed that cyclic ketones are capable of being condensed with acetone. He now reports²⁾, as the most important result of his recent researches, that he has succeeded in showing that when the cyclohexanones are condensed with acetone, the oxygen-atom of the cyclic ketone combines with the hydrogen of the acetone and is eliminated in the form of water, giving rise to unsaturated extra-cyclic ketones, which by reduction are convertible into saturated extra-cyclic

¹⁾ Berl. Berichte 29 (1896), 1597, 2955.

²⁾ Nachr. K. Ges. Wiss. Göttingen 1912. Meeting of 17th February.

ketones. It is probable that in the condensation-products which are originally formed the ethylenic bond is not in the semicyclic position, but occurs within the ring, or the bodies may present a mixture in which the second modification exceeds the first. It may be assumed that addition preceeds condensation, in which case the additive product must possess the formula I shown below, and a compound of this type may as readily be converted into II as in III. 1,3- and 1,4-Methylcyclohexanone and acetone gave rise to 1,3- and 1,4-methylcyclohexene acetone which were reducible by Paal's method into 1,3- and 1,4-methylcyclohexyl acetone.



In our last October *Report*, p. 146, we referred to the ketonic acid $C_{12}H_{20}O_3$ which had been prepared by O. Wallach¹⁾ from cyclohexylhexanone by oxidation with chromic acid in glacial acetic acid, and which he supposed to be a δ -hexahydrobenzoyl-*n*-valeric acid. Wallach has recently been able to prove the correctness of his supposition²⁾. He split up cyclohexylhexanone-*iso*-oxime by heating in a sealed tube with hydrochloric acid, and thus obtained an amido-acid which, when oxidised with potassium permanganate in faintly alkaline solution, yielded the keto acid $C_{12}H_{20}O_3$. The formation of this ketonic acid from the amido acid proves that the amido acid is ϵ -cyclohexyl- ϵ -amido-*n*-caproic acid and that for the ketonic acid the formula $C_6H_{11}CO(CH_2)_4CO_2H$ must be regarded as having been established. For from the amide of the ketonic acid Wallach obtained a ketoximic acid $C_6H_{11}\overset{\cdot\cdot}{C}(CH_2)_4CO_2H$ which was very



readily rearranged by means of phosphorus pentachloride. In the course of this reaction a compound was formed which was isomeric with the oximic acid used. This compound, when heated in a sealed tube with hydrochloric acid, was split up into cyclohexylamine and adipic acid. Hence it follows that the conversion-product of ketoximic acid must have the formula $C_6H_{11}\cdot NHCO(CH_2)_4CO_2H$: that the isomerisation must have proceeded as follows: $C_6H_{11}\overset{\cdot\cdot}{C}(CH_2)_4CO_2H \rightarrow C_6H_{11}NH\cdot CO(CH_2)_4CO_2H$;



and that the fundamental ketonic acid can only have possessed the structure $C_6H_{11}CO(CH_2)_4CO_2H$.

¹⁾ *Liebigs Annalen* 381 (1911), 102.

²⁾ *Ibidem* 389 (1912), 169.

Menthone. Some time ago G. Vavon¹⁾ described the reduction of carvone by hydrogen in the presence of platinum. By reducing *l*-menthone [$\alpha_{D}^{25} - 22,6^\circ$] by the same method, Vavon²⁾ has obtained a menthol with b. p. 208 to 209 $^\circ$; 98 to 99 $^\circ$ (13 mm.); $\alpha_{D}^{25} + 10,6^\circ$. The same menthol was obtainable from pulegone. Its rotation was low: $\alpha_{D}^{25} + 6,4^\circ$.

H. Stobbe and A. Rosenberg³⁾ have ascertained that when menthone is allowed to react with benzalacetophenone in the presence of sodium ethylate, it yields a ketone alcohol, m. p. 128 to 129 $^\circ$: $[\alpha]_D + 57,59^\circ$. It was impossible to determine exactly the structure of this compound: it is either a 2, 4-diphenyl-5-*isopropyl*-8-methyl-9-keto-4-hydroxybicyclononane or a 2, 4-diphenyl-1-*isopropyl*-6-methyl-9-keto-4-hydroxybicyclononane. The compound does not react with dimethyl sulphate, nor with acetic anhydride or benzoylchloride or with phenylisocyanate. This indifference towards the reagents in question on the part of a ketone alcohol is at first somewhat surprising, but it agrees with the experience of Dieckmann and von Fischer⁴⁾ that hydroxy compounds of exactly similar structure, namely the cyclohexanolone carboxylic esters, are equally incapable of being benzoylated.

So far it has been found impossible to unite other ring-ketones, such as *d*-fenchone or camphor, with benzalacetophenone or other analogous unsaturated ketones⁵⁾.

In one of our earlier *Reports* we mentioned a paper by O. Wallach on the decomposition of hydroaromatic ketones by heating with potassium hydroxide. Wallach had already previously discovered⁶⁾ that heating menthone oxime with potash gives rise to a decylic acid $C_{10}H_{20}O_2$. Recently the author⁷⁾ has again carried out the same experiments on a larger scale and has obtained thymol as a by-product. The phenol was identified from its phenylurethane (m. p. 103 to 104 $^\circ$), in addition to which the urethane was split off by careful heating, in which process thymol (m. p. 49 to 50 $^\circ$) was reconstituted. The acid reaction products consist chiefly of decylic acid (b. p. about 250 $^\circ$), to which an isomeride is probably admixed. It yields a methylester with b. p. 212 to 215 $^\circ$. The amide of the acid melts at 108 to 109 $^\circ$.

¹⁾ *Compt. rend.* 153 (1911), 68; *Report* October 1911, 150.

²⁾ It is not clear from the paper what was the source of the light used by Vavon.

³⁾ *Compt. rend.* 155 (1912), 286.

⁴⁾ *Journ. f. prakt. Chem.* II. 86 (1912), 226.

⁵⁾ *Berl. Berichte* 44 (1911), 967, footnote.

⁶⁾ See R. Georgi and A. Schwyzer, *Journ. f. prakt. Chem.* II. 86 (1912), 237.

⁷⁾ *Liebigs Annalen* 369 (1909), 98; *Report* April 1910, 181.

⁸⁾ *Liebigs Annalen* 296 (1897), 128.

⁹⁾ *Ibidem* 389 (1912), 194.

Camphor. It is well known that camphor has spec. rot. $[\alpha]_{D^{20}} + 43^{\circ}$ (10 p. c. solution in methyl alcohol). Instead of proceeding with the temperature precisely at 15° , it is practicable, according to R. Massy¹⁾, to work at ordinary temperature with a 10 p. c. solution in a 2-dm-tube and to convert the rotation ρ *t* thus read off into the rotation at $15^{\circ} = \rho t - 0,035 (t - 15)$. With $t < 15$ the correction-factor becomes positive.

A. Faucon¹⁾ has determined the influence of concentration and of temperature upon the specific rotation of camphor in carbon tetrachloride solution.

With a view of determining the density of camphor, H. Malosse²⁾ has prepared *p*-percentage solutions (*p* = 10 to 60) in 90 and 99 p. c. alcohol, acetone, methyl alcohol, benzene, ethyl acetate, olive oil, dimethyl aniline, acetic acid, and carbon tetrachloride and has estimated the density at 20° (compared with water at 4°). By transferring the values of *p* to the abscissa and those of d_{40}^{20} to the ordinata, density curves are obtained which, when carried out to *p* = 100, cross the ordinates placed at 100 at about 0,963, from which the density of 100 p. c. camphor is calculated as $d_{40}^{20} = 0,963$. This value deviates considerably from that which has previously been ascertained for *l*-camphor ($d_{40}^{20} 0,9653$).

Epicamphor. A simple method of preparing epicamphor (β -camphor), a body of which we reported the discovery in our *Report* of October 1911, p. 148, is described by J. Brecht and W. H. Perkin³⁾. The start from methyl bornylene carboxylate, which they convert, by the action of hydroxylamine hydrochloride and sodium methoxylate, into bornylene hydroxamic acid $C_{10}H_{16} \cdot C(OH) : N \cdot OH$ (m. p. 136° , m. p. of the acetyl compound 112°). This hydroxamic acid, when heated, yields epicamphor and ammonia. The sodium salt of the hydroxamic acid, when treated with toluene *p*-sulphonyl-chloride yields a syrupy mass. By treatment with of hydrochloric acid this syrup, when distilled with steam, yields 60 p. c. of epicamphor, m. p. 184 to 185° ; $[\alpha]_D^{20} - 58,24^{\circ}$, m. p. of the oxime 103° , of the semicarbazone 238° . When epicamphor is heated with bromine it gives rise to bromoepicamphor, m. p. 134° ; $[\alpha]_D^{20} - 69,3^{\circ}$. Reduction of epicamphor with sodium and alcohol results in epiborneol (β -borneol) (m. p. 182 to 183°) which is identified by its urethane, m. p. 82° . Possibly the epiborneol is not present in the pure state, but consists of a mixture of epiborneol and epio-borneol. By acting upon epicamphor with sodamide and isoamyl nitrite a mixture results of

¹⁾ *Bull. Soc. Pharm. Bordeaux* 1911, 453. Quoted from *Zeitschr. f. allg. chem. Supplement* Ver. 66 (1912), 306.

²⁾ *Compt. rend.* 154 (1912), 652.

³⁾ *Compt. rend.* 154 (1912), 1697.

⁴⁾ *Pract. chem. Rev.* 26 (1912), 56.

two isonitroso-derivatives $C_{10}H_{14}O:NOH$, which, by being recrystallised from light petroleum, can be separated into an α - and β -isomeride. α -Isonitroso-epicamphor is less easily soluble, and has m. p. 170° ; $[\alpha]_D - 201,9^\circ$. β -Isonitroso-epicamphor has m. p. 140° ; ($[\alpha]_D - 184,3^\circ$) and when heated above its m. p. is converted into α -isonitroso-epicamphor. When treated with formaldehyde and hydrochloric acid both isomerides yield camphoric acid imide (m. p. 244°). Reduction of β -isonitroso-epicamphor with zinc dust in alkaline solution leads to aminoepicamphor: m. p. 168 to 170° ; $[\alpha]_D + 30,15^\circ$.

Epicamphorcarboxylic acid, $C_{10}H_{15}O \cdot CO_2H$ is produced by the action of sodium or sodamide upon epicamphor in the presence of carbon dioxide m. p. 122° . It gives a green coloration with ferric chloride in alcoholic solution. Bromoepicamphor carboxylic acid melts at 148 to 150° with formation of bromoepicamphor.

In the investigation of β -camphor (epicamphor) and of certain halogen derivatives of camphor, L. Tschugaeff¹⁾ has arrived at the conclusion that the abnormal exaltation of the rotatory dispersion is probably a property of all camphor derivatives which contain the $C \cdot CO \cdot C$ -group.

Isocamphor. The *isocamphor* which has been described by Angeli and Rimini, and on the properties of which Wallach reported some time ago²⁾, possesses, as Wallach has discovered³⁾ in the course of the continuation of his investigations, an entirely different structure from that which had been assumed up to the present. When reduced by Paal's method, the *isocamphor* yielded a ketone which, when purified from primarily-produced semicarbazone, was found to possess the characters of dihydropinolone⁴⁾ (b. p. 211° ; $d_{20} 0,8885$; $n_D 1,4466$; m. p. of the semicarbazone 164°). Similarly, the properties of the alcohol $C_{10}H_{19}OH$, which is obtainable by reducing dihydroisocamphor, agreed entirely with those ascertained for dihydropinolol. Oxidation of dihydroisocamphor with hypobromite afforded an acid of which the amide had m. p. 164° and which suffered no depression of m. p. when mixed with the amide obtained from dihydropinolone. So far Wallach has not succeeded in clearing up the constitution of *isocamphor* itself. The fact that *isocamphor*, not only when reduced with sodium, but also when reduced by Paal's method, afforded dihydropinolone, rendered improbable a displacement of atoms in the molecule of *isocamphor* during hydrogenation. Nevertheless, the *isocamphor* oxime was also subjected to hydrogenation by Paal's method, and here

¹⁾ Bull. Soc. chim. IV. 11 (1912), 718.

²⁾ Comp. Report April 1911, 183.

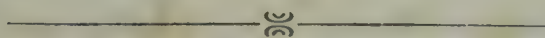
³⁾ Liebigs Annalen 392 (1912), 69.

⁴⁾ Comp. Report April 1912, 183.

SEMI-ANNUAL REPORT
OF
SCHIMMEL & Co.
(FRITZSCHE BROTHERS)

MILTITZ
NEAR LEIPZIG

LONDON * NEW YORK



APRIL 1912.

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List of abbreviations.

d = specific gravity.

d_{200} = specific gravity at 20° (in references from our laboratories uniformly compared with water at 15°).

d_{40}^{20} = specific gravity at 20° , compared with water at 4° .

α_{D200} = optical rotation at 20° , in a 100 mm. tube.

$[\alpha]_D$ = specific rotation.

n_{D200} = index of refraction at 20° .

Sol. p. = solidifying point.

M. p. = melting point.

B. p. = boiling point.

n = normal.

Acid v. = acid value; ester v. = ester value; sap. v. = saponification value

g. = gram; cc. cubic centimeter; mm. = millimeter.

Temperatures are uniformly given in degrees Centigrade.

The strength of alcohol, if not otherwise indicated, is given in per cent. by volume.

The development of German industry — especially in our own branch of Chemistry —, has made further important progress in the year 1911, and the decided strengthening of the commercial situation which has now been noticeable for two years has stamped upon the past twelvemonth, as upon that which preceded it, the imprint of an allround wholesome and satisfactory economic period. The general retrospect would doubtless have been more favourable still if the close of the commercial year had not been seriously disturbed by difficulties and complications in foreign politics, complications of which in some instances the full extent could only be surveyed after they had been removed. The negotiations concerning Morocco, which gave rise to all manner of grave apprehensions for the relations between Germany and France, the acute tension, in the course of the autumn, between Germany and Great Britain, the Italian war with Turkey, which might easily have led to serious disturbance of the peace of Europe, and finally the troubles in China and in Persia were incidents which at times called forth a certain feeling of nervousness which affected the whole commercial life of Germany, and this of course was not without its effect upon the development of trade and industry. To these disturbing elements must be added the general rise in food-prices (partly the result of abnormal climatic conditions), which seriously impaired the purchasing-power of the whole nation, especially during the second half of the year, while the chronic labour-unrest also exercised a paralysing effect upon the spirit of enterprise in many branches of industry. In respect of the last-named feature we fully endorse the following passage in the Report of the Hamburg Chamber of Commerce: "These conditions not only weigh heavily upon German industry as a permanent danger; they also impede its further extension and development, and afford fresh proof of the necessity of closer union between the work-givers with the object of defending themselves against an aggression which is becoming well-nigh insupportable". It is true that during the past year Germany has happily remained free from great strike-movements, but it is evident that labour-disturbances such as those which have been experienced in France, and such as the coal-strike in Britain, which for several weeks

¹⁾ The introduction to the present Report and the Commercial part were written during March.

paralysed the whole industrial life of this neighbour-country, must in directly also injure German industry. When in a country like England which is such an important market for German products, business is practically at a standstill during a longer or shorter period, it is obvious that our export-trade cannot remain unaffected. In the German coalfields, unfortunately, the British coal-strike has also provoked disturbances, which however, have subsided more quickly than those across the North Sea.

The strength of the German money-market was put to a severe test last autumn, when the uncertain political situation resulted in the sudden withdrawal of funds due to French and British creditors. The sensational reports, partly maliciously inspired, which appeared in certain foreign papers at the time were powerless to shake our money-market, notwithstanding the fact that simultaneously it had to meet increasing claims on the part of German traders, and the success with which it stood the trial has decidedly increased foreign respect for the financial power of Germany.

The foreign trade of the German Empire in the year 1911 shows the following totals: —

Imports 9544,8 million Marks, compared with 8930,0 million Marks in 1910,
Exports 8111,8 " " " " 7474,6 " " " 1910.

A comparison between the values of the imports and exports of the three principal commercial countries of Europe bears eloquent witness to the satisfactory development of Germany's foreign trade. The figures for the years 1910 and 1911, in million Marks, were as follows: —

Germany	{	Exports in 1911 8 111,8,	Imports 1911 9 544,8	} + 1242
		" " 1910 7 474,6,	" 1910 8 930	
United Kingdom {	" " 1911 9 222,	" 1911 13 815	} + 531	
	" " 1910 8 737,	" 1910 13 769		
France	{	" " 1911 4 938,	Imports 1911 6 529	} + 740
		" " 1910 4 988,	" 1910 5 739	

Closer consideration of the above figures shows that the foreign trade of Germany has grown at a materially higher rate than that of either Britain or France. A surprising fact is the notable drop in French exports, the increased trading-turnover of the Republic being entirely due to the rise in imports. We should be exceeding our scope were we, in these pages, to trace the causes that have brought about a result which is the more noteworthy in view of the enactment in the year 1910 of increased protective duties, from which another outcome would certainly have been expected.

The German chemical industry, and in a more restricted sense the industry of essential oils, essences and artificial perfumes, has had its

full share of the advance in German export trade and, as will be seen from the figures given below, our branch has no cause for dissatisfaction with the results achieved: —

German foreign trade in essential oils¹⁾

	Imports	Exports
In 1911:	1 251 500 kilos	599 300 kilos
" 1910:	1 524 300 "	547 600 "
" 1909:	755 800 "	512 600 "
" 1908:	911 300 "	390 800 "
" 1907:	1 498 600 "	491 700 "

German foreign trade in artificial odoriferous substances²⁾

	Imports	Exports
In 1911:	17 300 kilos	492 800 kilos
" 1910:	17 900 "	428 800 "
" 1909:	16 100 "	417 100 "
" 1908:	11 300 "	280 000 "

It will be seen from these statistics that the imports of essential oils as well as of artificial odoriferous substances have fallen off in a not inconsiderable degree, while it is satisfactory to note that the exports of the former have risen by over 50 000 kilos and of the latter by as much as 64 000 kilos. The German artificial perfume industry has a right to be particularly proud of this result, because it has been achieved in a branch in which foreign, and especially Swiss, competition is extremely keen. As in previous years so in 1911 a very important share of the total imports of essential oils falls to the account of our firm. Our receipts of camphor oil alone amounted to about one-fourth of the entire imports.

In point of fact our business during the past year has been marked by a steady and healthy increase in turnover, and by such briskness in almost every consuming market that from the very commencement of the year, and in spite of the incidents which, as stated above, disturbed the course of trade at intervals, a favourable financial result appeared to be assured. The already excellent demand for our manufactures in almost all consuming markets was further assisted by the rising tendency of certain important articles, such as menthol, sandalwood oil and — towards the close of the year — the Italian essences, with the result that our business developed to such a degree as to throw completely in the shade even the record year 1907. We certainly have no cause to draw other than a most favourable picture of our operations in the year 1911, and we are convinced that every firm in our branch of industry which

¹⁾ Statistisches Warenverzeichnis No. 353 b/c.

²⁾ Statistisches Warenverzeichnis No. 354.

has built up its business on the same sound principles that govern ours will have had a similar satisfactory experience.

The first two months of the present year have also been characterised by an animated demand and an increasing turnover, and there is every prospect of continued favourable development, provided peace be maintained. By increasing the number of steam-boilers in our works to 23 with an aggregate heating-area of 2500 sq. meters, we have prepared ourselves for a further expansion of our output, after having been compelled to raise our capacity of production to its highest power, by introducing the day- and night-shift system in some of our principal departments, thus securing continuous working.

Before passing to our customary detailed review of the various markets we are compelled, to our regret, to record the disagreeable fact that during the past year the malpractice of adulteration has attained dimensions never previously known in our branch. Perhaps the most eloquent testimony on this subject is afforded by the numerous occasions on which our testing-laboratory has been asked to pronounce an expert-opinion. The alarming extent to which the ever-advancing scientific investigation of the constituents of the essential oils is utilised by dishonest traders to practise cunning forms of adulteration, especially such as are designed to represent their goods as of better quality than they really are, is positively astounding. In the great majority of cases the primary methods of examination, as for instance the determination of specific gravity, of solubility and of optical rotation, and even the simpler chemical tests, such as saponification and acetylation, no longer suffice to trace malpractices of this kind, and it is necessary to carry out the various investigations in all their complicated details in order to reveal the inferior nature of the artificial mixtures. We regard it as a particularly painful matter that firms should be found which are not ashamed openly to offer for sale preparations that appear to be suitable for the manufacture of such ingenious sophistications, and to offer them on the express ground that the preparation serves some such purpose as that of apparently increasing the ester-content of an oil. We have on previous occasions quoted several instances of this practice, which is carried on sometimes by letter and sometimes through travellers. That German firms should take part in such a traffic is the more deplorable because it has been one of the chief merits of the German research-chemists that for many years they have successfully laboured to raise the whole of the essential oil trade to a higher level by establishing suitable methods of examination, and it must be obvious that for us, who have been pioneers in this field of research, the existence of such malpractices must be particularly unpleasant. Quite recently we were informed of a case in which a German firm which makes pretensions to rank among the first and most important in the chemical industry was offering in various places abroad preparations of which the

purpose is fictitiously to increase the ester-content of essential oils. The letter in which the offer was made was sent to us; the name of the preparations we suppress in the interest of honourable trading. We hope that the repeated discovery by us of such regrettable incidents will at length bring about a change in this state of things, for in the alternative we shall certainly take an early opportunity of publicly pillorying the firms concerned, whose original offers are in our possession.

A word, also, on the subject of the deplorable cases of methyl alcohol poisoning. We have always advocated the view that the employment for purposes of human consumption of this substitute for ethyl alcohol is unjustifiable, but we have also repeatedly pointed out that there are grave objections to its use in the manufacture of perfumes and cosmetics, notwithstanding the fact that these articles are for external use only. We know that important methyl alcohol manufacturers are in the habit of recommending their preparation for the last-named purposes, and in order to guard our business-friends against unpleasant experiences we expressly warn them not to entertain such suggestions.

Our Branch-Office at Bodenbach has obtained its well-deserved share of last year's business-successes, our sales in the Austro-Hungarian Monarchy showing a considerable increase. In the spirits-department, however, the conditions were far from favourable, for to the burdens and obstructions which have beset this branch of trade in the past few years there is now to be added the Spirit-Trust, while the threatened Spirit Taxation Bill contributes to render the situation far from rosy. Operations have been started in the meantime in the extension of our Bodenbach works, to which we have already referred on a previous occasion, and among other processes of manufacture we have commenced the preparation on a large scale of sugar-colour from refined sugar. We take this opportunity of again calling the attention of our Austrian and Hungarian friends to this article.

Our relations with our customers in France have developed in a highly satisfactory manner, in spite of the increased Customs Duties imposed in 1910, which so seriously hamper the importation of our products. German exports to France in the year 1911 showed an increase in value of over 88 million Marks, and although it need scarcely be said that the share of our branch of industry in this increase is a very modest one, we are pleased to be able again to place upon record the steady and wholesome expansion of our relations with our Western neighbour. The political tension, which last autumn might easily have led to a catastrophe, has again given place to a more amicable disposition, except as regards a persistently Chauvinistic section of the French press, and there is no cause for believing that the prospects of a return of restful conditions and mutual confidence, even in a political sense, are unfavourable. The demand from France last year was not limited chiefly to those costly

artificial perfumes which give their characteristic stamp to so many French perfumery-specialities, but all other articles of our manufacture were likewise in strong request. The troubles with the Custom-House, to which we have already previously referred, still persist, although here, too, cannot be gainsaid that there has been some improvement.

Our turnover in Great Britain has again experienced a marked increase in 1911, our London branch having been fully occupied throughout the year. In view of the many vexations that have beset trade in this country in the past year this result must be regarded as thoroughly satisfactory, the more so because a state of political and economic quiescence, such as is imperative to salutary commercial development, appears unfortunately so far as Britain is concerned, to belong to the realm of the future. Apart from the state of political tension, sedulously fostered by a section of the press both in Germany and in the British Isles, which in the second half of 1911 was at times so great as to give rise to fears of a rupture between the two nations, and of which the after-effects are unfortunately not yet wholly dispelled, the internal political imbroglio, to which reference has already been made on previous occasions, is by no means cleared up. The Irish Home Rule question continues to excite the minds of the people and makes it difficult for Parliament to settle down to quiet work. There is no doubt that this state of things will persist until this vexed question has been disposed of in some way or other. To this must be added the strikes which are forever breaking out in fresh places, and among which the gigantic national colliers' strike which broke out in the beginning of March constitutes the record, inasmuch as it involved the voluntary cessation from work of a million coal-miners, and has drawn into common suffering nearly 600 000 workers in other industries, because the factories which employed them had to close down for lack of coal. Although the end of this calamity is now at hand, the wounds inflicted by such a national catastrophe are far less easily healed than given. Hence the prospects for the immediate future could hardly be regarded as rosy were it not that Britain's powerful financial position in the world's commerce is a favourable factor which must not be under-estimated. Notwithstanding all the great internal difficulties of the country the trade statistics continue to show steadily increasing imports and exports (see p. 6).

With regard to trade with British India there is, generally speaking, little or no news to be reported. The turnover increases within normal limits, but this vast, although proportionately poor, market is only slowly beginning to recognise that the buyer who is everlastingly seeking to buy low-priced goods will usually find, on examining his purchase and comparing its value, that he has made a thoroughly bad bargain. Over and over again we encounter quotations which show only too clearly the kind of rubbish to which "cheap competition" has accustomed the native trader, who very often is a most credulous person and possesses only the most

superficial acquaintance with the means of judging the value of goods in our branch of industry. To this must be added the unsound practice by which indents from India to European export-houses are almost invariably placed on the basis of price alone, that is to say, unless special sources of supply are indicated, the export-firm concerned simply sends round a request for "lowest quotations" to a dozen or so of manufacturers, and he who quotes least obtains the order. It is evident that under such conditions British India is bound to become the staple-place for rubbish of all descriptions, and European firms in that country have already denounced this state of things in the press without stint. But even here daylight is breaking, and we are glad to be able to state that the better elements among the traders and consumers have become much more appreciative of first-class, pure qualities than was the case a few years ago. But a great deal of pioneering-work still needs to be done to bring consumers at large to a sense of the importance of pure wares.

The Coronation-Durbar, which was celebrated with enormous pomp and a truly Oriental gorgeousness, has passed off without untoward incidents. The elevation of Delhi to the rank of the Capital of India was the most important episode of these festive days. This step, the sequel of conditions of which the discussion lies outside our scope, was entirely unexpected, and naturally created an unpleasant impression in Calcutta, the present Capital. But it would appear that city has quickly accommodated itself to the new order of things, for although it may be loath to be deprived henceforth of the splendour of the Vice-Regal Court, that removal cannot depose it from its place as the chief commercial centre of British India.

The craze for cheapness, to which we referred above, also remains an unfavourable factor in business-relations with Australia. It is true that things are not quite so bad here as they are in the Indian trade, but it needs continuous exertion on the part of respectable firms successfully to combat this deep-seated evil, especially because an inevitable result of such traffic is that the goods supplied are invariably of low quality, and bound sooner or later to disappoint the buyer bitterly. This fact, although it should be self-evident, cannot too often be brought to the notice of those buyers whose one and only guide is lowness of price, who regard the test of quality as a matter of subordinate concern, and who, in fact, consider it almost their duty invariably to prefer the lowest quotation. For the rest there is nothing new to report concerning Australian trade, the turnover being steadily although slowly on the increase. The economic conditions upon which we commented in our last Report apparently continue to hamper the normal development of the entire Continent; a fact which is readily understood by those who know Australian conditions from personal observation. The disinclination of large capitalists to invest money in new industrial undertakings in that country while these

conditions prevail scarcely requires comment: one can only express regret that the development of this highly-promising and otherwise prosperous land should be retarded by such artificial checks as have been imposed there during the past decade or so.

There has been very little alteration since last autumn in the economic condition of Spain. The bad harvests of 1909 and 1910 have been followed in 1911 by good, and in parts even excellent, crops, especially of wine and oil, but the effect of these is hardly perceptible owing to the critical state of Spanish politics. In the first place the Morocco-adventure of which the end seems to be far distant, is always calling for fresh sacrifices of life and gold. The Liberal party still holds the reins of Government, but such difficulties have been thrown in the path of the Prime Minister by the Conservatives that he has twice offered his resignation.

Pesetas	Imports from :		Exports to :	
	1900 Million	1909 Million	1900 Million	1909 Million
Germany	77,8	114,5	31,9	48,4
France	147,4	198	217,3	238,9
United Kingdom	249,3	206,2	276,8	267,1
Belgium	43	32,2	25,3	36,2
Portugal	41,9	48,2	36	48,4
Russia	42,6	26,3	—	—
Italy	24,2	93,9	24,4	42,6
Holland and the rest of Europe	74,3		42,2	88,1
Total:	700,5	719,3	653,9	769,7
Increase:	about 3%		about 17,5%	

since last Autumn, and has only been induced to continue at his post by the personal intervention of the King. Naturally, such an unsatisfactory state of things is not exactly conducive to the revival of trade and industry. In spite of this both the imports and exports have increased during the past decade, as will be seen from a comparison of the figures for the years 1900 and 1909 which we quote from an article in the *Heraldo de Madrid*. Statistical data of Spanish commerce are somewhat scarce, and we give an abstract of the article in question, because the figures give an approximate idea of the facts. They show that the direct export trade from Germany to Spain has increased between 1900 and 1909 by 36 700 000 Pesetas, or nearly 50%! In connection with this it must be remembered that large quantities of German goods are imported by way of other countries, especially France and Great Britain, and appear in the statistics as French or British goods.

The U. S. Consul at Malaga¹⁾ reports that about twelve years ago the preparation of essential oils was taken up there, and although, judging by the value of the output, the business is one of the less important of the new branches of industry which have arisen in the locality, it is apparently one of the most successful and promising. There are at Malaga five works engaged in the preparation of essential oils, and two of these have been equipped with up-to-date steam-distilling plant and are managed by German chemists. The whole of the output is exported, and all the processes of distilling, hand-pressing and "enfleurage" are carried out on strictly scientific lines. The industry is remarkable for the variety of its productions, among which are the following: oils of anise, lemon, geranium, neroli, pennyroyal, rosemary, spike, red thyme and juniper. Although herbs and flowers for the preparation of essential oil are very little grown, there is no scarcity of raw material, and distilling can be carried on all the year round.

The local custom-house statistics show that the productivity of the chemical industry of the district has grown considerably within the past three years. In the year 1908 the exports amounted to about 38260 kilos, in 1909 to 89800 kilos, and in 1910 to as much as 145130 kilos. The principal part of the exports is absorbed by France, Germany, Great Britain and Cuba. Artificial essential oils are also being prepared on a small scale.

Russia, which is an important consuming-market for our articles, affords no occasion for special comment. It is only necessary to call attention to the fact that in this country competition is very keen, and is not always conducted on honourable lines.

There is nothing of material importance to record with regard to business in the Balkan-States. Roumania is steadily developing into a market for our manufactures which is worthy of serious attention, and the conditions of credit in this country have ameliorated; confidence in Turkey, on the other hand, will not be fully restored until the regrettable war with Italy has come to a termination. Unfortunately there is at present no sign of this. According to the *Reichs-Gesetzblatt*, the official Gazette of Germany, the Commercial Treaty between Turkey and Germany of 26th August 1890, and the Supplementary Agreement of 25th April 1907 belonging to that Treaty, both of which were due to expire on March 13th, have been provisionally extended by mutual agreement until 24th June 1914. In Servia there has been a very gratifying development in the sale of articles of our branch, and the knowledge necessary for the proper appreciation of our standard of quality is gradually making way there. We quote from the *Chemische Industrie*²⁾ the following brief particulars concerning the business in essential oils and perfumes in Servia in the

¹⁾ Daily Consular and Trade Reports, 10. 2. 1911.

²⁾ Chem. Industrie 35 (1912), 83.

year 1910: The value of the imports of articles falling under this heading in 1910 was 219519 Dinars, compared with 152888 Dinars in 1909. The articles themselves included: essential oils from wood tar and rubber (?), resin oil, spirits of resin, turpentine oil and camphor oil, together 65763 kilos, valued at 42337 Dinars, of which 50614 kilos came from Russia and 12423 kilos from Austria-Hungary; essential oils of juniper, laurel, jasmine, almond, rosemary and bergamot, together 12736 kilos, valued at 14187 Dinars, all of which was imported from Germany; fine essential oils of rose, lily of the valley, violet and orange-flowers, valued at about 25000 Dinars and also imported from Germany; artificial perfumes, of which the importation is small, also from Germany. Of perfumery 5936 kilos, valued at 59946 Dinars, were imported almost entirely from Germany; various cosmetics (6165 kilos, valued at 56804 Dinars) came from Germany (3481 kilos) and France (1927 kilos). It will be seen from these figures that the sale of articles of our branch in Servia has developed quite satisfactorily.

Nothing remains to be said in the present Report with regard to the other European markets.

The position of affairs in Egypt is rather less favourable than last year, for this country is primarily dependent, for good or evil, upon its harvest. According to the Customs Statistics the cotton-crop of 1910/11 has yielded a return of £ 26550000, whereas the estimated export-value of the 1911/12 crop is only £ 19500000. Such a falling-off must be the heavier to bear because the country has not yet quite recovered from the crisis of 1907. As a result the conditions of credit once more leave a great deal to be desired at present. According to a report published by the German Ministry of the Interior¹⁾ the fact should be borne in mind that Egypt itself has been unable to provide the capital required for the rapid growth of her economic life during the past decade, and has been mainly dependent upon foreign credit. If, therefore, the process of restoration to economic health is to take a normal course it is of prime importance that this credit should not be shaken, and especially that with the moderate crop of the present year the credits should be renewed until the gathering of the new crop.

The Bulletin of the French Chamber of Commerce at Alexandria²⁾ publishes an interesting article on the importation into Egypt of toilet-preparations and perfumes. We reproduce this article below in the expectation that it may convey useful hints to some of our friends engaged in the perfumery-industry.

According to statistical returns, the imports into Egypt of powders, cosmetics, extracts, toilet-waters and face-paints during the past seven years have reached an average value of £ 44000, of which one-half falls

¹⁾ Nachrichten f. Handel u. Industrie 1911, No. 146, p. 2.

²⁾ Chem. Industrie 35 (1912), 699.

to the share of France. There is no doubt that this figure does not represent the actual value of the consumption, for the leading druggists and pharmacists in the large centres of Cairo and Alexandria generally prepare their own Eau-de-Colognes and toilet-waters, mouth-washes, dentifrices and scents, especially because by doing so they are able to supply at much lower prices. Hairdressers, likewise, rarely use articles prepared in Europe; they lay in their requirements for the most part from the native druggists, or they prepare them themselves. The extremely low cost of alcohol explains this practice, for it enables the natives to manufacture the goods more cheaply than they could buy them ready-made. From Britain the principal imports in this branch consist of Eau-de-Cologne, cosmetics, hair-restorers and tooth-pastes. English perfumes, on account of their costliness, are only used to a small extent, chiefly by Europeans

	1903	1904	1905	1906	1907	1908	1909
Great Britain	4393	5022	4558	4946	4776	4984	6467
Germany	8138	8622	6916	5919	7077	4949	4687
Austria-Hungary	1508	2966	2261	2012	2918	1061	860
Belgium	112	188	87	127	141	141	196
China and Eastern Asia	402	—	—	—	—	—	24
U. S. America	785	1271	1096	1343	1709	1448	991
France	19790	23073	21566	29452	33638	24179	25059
Greece	41	83	245	313	332	168	298
Holland	—	—	—	359	—	—	—
Italy	667	847	617	771	1421	792	941
Russia	—	44	21	—	—	—	—
Switzerland	13	19	—	17	—	36	54
Turkey	2182	2642	2683	2635	3104	3158	2913
Other countries	15	—	52	—	—	—	—
Total:	38047	44777	40102	47894	55116	40916	42490

and by natives of high rank. German perfumes were unknown in Egypt 25 years ago, but to-day Germany supplies one-tenth of the total imports. The German manufacturers have not only appointed local agents, but they work the whole country systematically by commercial travellers and thus gradually increase their sales year by year. The high-water mark of German imports, however, was reached in the years 1903 and 1904. From that time until 1909 it fell by 50% in favour of French preparations, which have everywhere replaced the competing German articles. German goods mostly go to the Arab consumers in the villages and towns; they consist of attractive but cheap wares of all sorts and descriptions, but especially of Eau-de-Cologne, lavender-water and preparations for the mouth and teeth. The imports from the United States in the year 1892 reached a value of over £ 2000; but this figure was not maintained and in 1909 the

value of imports from this quarter had fallen to £ 991, consisting mainly of Florida water, hair-restorers and a few extracts. The table below shows the proportionate shares of the various countries interested in the import trade for the years 1903 to 1909, the figures being given in £ sterling. The report suggests that the best way to secure a foothold in the Egyptian perfumery-market is to make a thorough canvass of the customers by commercial travellers, who should call on the buyer again and again. In order to reduce the expense of this method of procedure it is desirable to appoint travellers who represent several firms. The principal customers are druggists, pharmacists, jewellers, hairdressers and bazaars. As advertising is not expensive, this method of propaganda is also to be recommended, especially because the advertisements in the daily papers are read. The best seasons for travelling are September-October and March-April.

Our New York friends report on the business in the United States as follows: —

“The general prospects for business in 1912 cannot be pronounced as very promising. Labor troubles, trust prosecutions, presidential election and the apprehension of quite radical changes in the Tariff, all constitute a menace to the quiet and normal development of trade. True enough, we have the labor troubles in common with Europe, but they assume a more passionate and uncurbed character here on account of the almost fanatic attitude of the labor unions against the capitalistic interest. In Europe the disturbing factors may lie more in the complications resulting from frictions in the foreign policy, here the instability of our interior conditions causes unrest and anxiety.

The Overman Bill, to which we referred in our last Report, and which in fact is equivalent to a radical revision of Schedule A (chemicals and drugs) has passed the House of Representatives by a Democratic vote of 179 against 127 dissenting Republicans and is now before the Senate. Here the Bill will be referred, in the routine way, to a committee which will hold the customary public hearings. These will serve the purpose of delaying any decision beyond the term of the presidential election, as it is absolutely unlikely that any political body would be willing to assume the responsibility for such a decisive measure and compromise itself during a presidential campaign.

The final fate of the Bill, which if adopted would seriously affect our line of merchandise, will then depend upon the composition of the new Legislature, but there is little probability that the principle underlying the present Bill, to levy duties upon raw materials, while reducing the rates upon manufactured articles at the same time, will ever be adopted by a majority of both Houses.

Though serious complaints are coming forth from several branches of industry, evidently due to the tinkering with the Tariff and the above

mentioned labor troubles, there is no reason for complaint in our line of business.

The year 1911 has again brought a very considerable increase in the volume of our business over the preceding year and, though on account of keen competition, the margin of profit did not grow in the same proportion as the volume of business, the year must, nevertheless, be pronounced as a very successful one.

Referring to the business prospects for the current year and judging from the amount of contract business closed during the first months of 1912, all indications would again point to a substantial gain over the good results attained in the preceding year.

The unfavorable crop conditions for many of the important raw materials affecting our line, rendered the business during the Fall and Winter months of 1911 and 1912 rather troublesome and unprofitable, as the extremely high prices for oils of lavender, geranium and bergamot, for instance, interfered seriously with the traffic in these staple commodities.

In regard to our trade with the Dominion of Canada, the expectations expressed in our last Report with reference to the Reciprocity Bill were not fulfilled. This apparently disappointing outcome, however, did not interfere with a further satisfactory development and extension of our business in this rapidly growing territory, which affords a constantly increasing outlet for goods in our line.

We consider the policy of our business to which we have adhered during a period of over forty years, and which has been practically sanctioned by the enactment of the Pure Food Law, as the sound foundation upon which we expect to further build and enlarge our business by continuing to advocate the use of pure products in preference to cheaper and adulterated goods."

The usual table supplied to us by our friends showing the exports from and imports into the United States of essential oils, will be found on p. 18.

The conditions prevailing in Mexico are the reverse of cheerful, but it is not difficult to understand why it is that this market, in which up to the present our goods have been able to boast an increasing sale, has not shown the expected further development last year. It cannot be denied that the failure of General Reyes' counter-revolution has somewhat calmed the feelings of the people, but the danger from this movement had hardly been averted when a new trouble arose which previously had attracted scarcely any attention. This is the steady growth of brigandage, which, having been allowed to go undisturbed in its commencement, has now become a formidable danger to the country, the States adjoining the Federal District, and lying therefore at the very gates of the capital, being the most infested. Up to the present all the efforts of the Government

**Value of imports and exports of essential oils into and from the U. S. A
in the second half-years of 1911 and 1910.**

		Imports				Exports			
		1911	1910			1911	1910		
		\$	\$			\$	\$		
July	{	Duty-free	165 038	147 970	July	{	Peppermint Oil	9 190	12 640
		Dutiable	66 848				47 281	Other indigenous oils	32 323
August	{	Duty-free	196 190	150 607	August	{	Foreign oils, duty-free	3 709	4 138
		Dutiable	53 467				60 037	" " dutiable	7 746
Sept.	{	Duty-free	139 037	110 378	Sept.	{	Peppermint Oil	25 864	12 753
		Dutiable	56 127				36 999	Other indigenous oils	24 636
October	{	Duty-free	164 169	130 909	October	{	Foreign oils, duty-free	1 021	3 208
		Dutiable	73 224				55 232	" " dutiable	5 711
Nov.	{	Duty-free	180 190	189 226	Nov.	{	Peppermint Oil	74 193	54 653
		Dutiable	61 707				70 103	Other indigenous oils	27 083
Dec.	{	Duty-free	199 591	159 463	Dec.	{	Foreign oils, duty-free	2 877	3 320
		Dutiable	73 924				77 532	" " dutiable	2 839
	{	Duty-free	164 169	130 909		{	Peppermint Oil	62 633	60 843
		Dutiable	73 224				55 232	Other indigenous oils	27 332
	{	Duty-free	180 190	189 226		{	Foreign oils, duty-free	1 815	2 348
		Dutiable	61 707				70 103	" " dutiable	4 800
	{	Duty-free	199 591	159 463		{	Peppermint Oil	64 266	26 443
		Dutiable	73 924				77 532	Other indigenous oils	21 029
	{	Duty-free	199 591	159 463		{	Foreign oils, duty-free	7 359	4 930
		Dutiable	73 924				77 532	" " dutiable	2 430
	{	Duty-free	199 591	159 463		{	Peppermint Oil	46 014	26 073
		Dutiable	73 924				77 532	Other indigenous oils	26 627
	{	Duty-free	199 591	159 463		{	Foreign oils, duty-free	623	4 200
		Dutiable	73 924				77 532	" " dutiable	2 030

Total value of imports in the 2 nd half-year 1911	\$	1 429 512
" " " " " " 2 nd " 1910	"	1 135 737
" " " " " " whole year 1911	"	2 864 251
" " " " " " " " 1910	"	2 446 716
Total value of exports in the 2 nd half-year 1911	\$	485 050
" " " " " " 2 nd " 1910	"	405 446
" " " " " " whole year 1911	"	798 484
" " " " " " " " 1910	"	675 030

to administer proper chastisement to the bandits have failed, as the government troops are not sufficiently familiar with the country and the rebels are abetted by the rural population. Discontent is growing daily among the lower classes, and the same people who acclaimed President Madero at the time of his entry into the capital are gradually being converted into his enemies, for few of the hopes entertained of him have been fulfilled, and the President is quite unable to carry out all the promises he has made. Unfortunately an anti-foreign movement is again beginning to show itself; a very grave sign indeed, which during the Revolution led to deplorable excesses, such as the horrors of Torreón, Covadonga and other

places, some of which remain unrevengeed until this day. Is it surprising, in these circumstances, that capital, nearly all of which is owned by foreigners, is very chary of investing in new undertakings in Mexico? It is earnestly to be hoped that there will be an improvement in the situation at an early date, so that the achievements of the Revolution, which has cost so much in blood and treasure, may at length be turned to the true advantage of the country.

If an inference were drawn from the good harvests of the past few seasons and from the extremely favourable sugar-prices, it would be fair to prognosticate a thoroughly satisfactory state of business in Cuba. Unfortunately this would be a false conclusion, for all hopes are disappointed by the fatal political troubles, which appear to have no end. Recent minor revolutionary risings have all been suppressed in good time, but a much more serious political conflict has now arisen. The veterans of the revolution of 1897 have made of the Government a demand which it cannot possibly grant; that is to say, the filling of all official posts by their partisans. How serious is the state of affairs may be gathered from the fact that the United States have already held out an emphatic threat of interfering for the third time — which would probably be the last. For the moment everything appears to be quiet again, but the fire continues to smoulder beneath the ashes, and is likely to break out with renewed intensity before long. Added to this there is universal dissatisfaction with the government of General Gomez.

A good idea of the economic position of Brazil (a country which takes the first rank among the South American markets for our manufactures, especially as regards artificial odoriferous substances), may be gathered from the annual report of the Deutsche Ueberseeische Bank. It is there stated that the Northern parts of the Republic, which are largely dependent upon the export of rubber, have suffered so severely from the fall in rubber-prices that the Government has been compelled to have recourse to exceptional measures (such as the abolition of customs duties on all tools and materials used in the collection and cultivation of rubber), for relieving the at times critical situation of those who are connected with the rubber-trade and -industry. On the other hand those parts of the country which are interested in coffee-growing, especially the State of São Paulo, have been brilliantly prosperous. Hence the falling-off in the rubber-exports has been counterbalanced by the increased value of the coffee-shipments and it is therefore probable that the commercial balance of Brazil will show a considerable excess of exports over imports for the year 1911. The statistical returns for the first 9 months of the year 1911, compared with the same period of 1910, show the following result:—

	Exports	Imports
1st January to 30th September 1911 . . .	£ 43 531 157	£ 38 662 620
1st " " 30th " 1910 . . .	£ 44 567 555	£ 34 088 068

This excess in value of exports, in conjunction with the uninterrupted influx of foreign capital in the form of State-loans, Federal-loans and City-loans, the acquisition of mortgages, shares and debentures in Brazilian undertakings, and the supply of materials for public and private buildings and for railways, has kept the rate of exchange for 90 days' acceptances on London at over 16 d. almost throughout the year, and has kept the fluctuations down to a very limited range, between 16 d. and 16¹/₄ d. whereas in the year 1910 the Brazilian rate of exchange fluctuated from 15¹/₁₆ d. to 18¹/₄ d.

The Brazilian Government is continuing its broadly-planned policy of opening-up the country. It has further extended its railway-system and has taken in hand a series of new and important lines in several States including Bahia, Ceará, Santa Catharina and Paraná. The energy displayed by the Government in rapidly increasing the means of communication and in carrying out new harbour-works and public-health undertakings on the widest scale throughout the vast extent of the Republic brings with it as a matter of course an urgent need of capital, and leads to a succession of fresh loans in the country itself and abroad.

In the neighbouring Republic of Uruguay trade has expanded in a satisfactory manner, and under its new President the social development of the country has taken a long step forward. As it is fair to assume that the new Government will continue to display a sound understanding of the economic needs of the country the continuance of favourable prospects may be looked for, always presuming that these bright hopes are not again brought to naught by a failure of the harvest. The following figures indicate the growth of imports and exports in the course of the past year: —

	Exports	Imports
1911 . . .	\$ 44 536 000	\$ 43 481 000
1910 . . .	\$ 43 700 000	\$ 41 151 000

The sale of our manufactures in Argentina continues to present a cheerful picture. The commercial situation of the country has further improved during the winter, if not strikingly, at any rate in a degree commensurate with the favourable crop prospects. The area under crop has been considerably extended, and the maize-crop in particular promises to yield a splendid return, judging by the estimates at present available. According to a report published by the Argentine Department of Agriculture, the total value of the crop of cereals and linseed is computed as follows: —

	1910/11	1911/12
	Pesos Gold	
Wheat.	140 000 000	174 000 000
Linseed	49 000 000	51 000 000
Oats	15 000 000	25 000 000
Maize	22 000 000	150 000 000
Total	226 000 000	400 000 000

This means a surplus of 174 000 000 Pesos as compared with last year.

The fact must be taken into consideration that the stocks of all imported articles are still very heavy and it is probable, therefore, that the actual revival of the export-trade to the Argentine will remain in abeyance for some little time. The difficulty with Italy appears to have been removed, for since the Argentine Congress has decided to abrogate the special sanitary measures against Italian vessels, the abolition of the Italian decree against emigration to Argentina, if not already actually carried out, may be expected in the near future. According to a communication by the German Consulate-General at Buenos Ayres, dated 13th January 1912, the total value of Argentine industrial products in the year 1911 exceeded 4000 million Marks. This increasing national production is a factor which can no longer be left out of account in considering the general economic balance of the country, and which will probably result in the commercial balance of Argentina showing for the year 1911 an excess of exports over imports. "Taking everything into consideration", the report concludes, "the country looks forward with confidence to the year 1912".

The conditions of export-business to Chili have been quite favourable in 1911, for the activity in the nitrate of soda trade has infused new vigour into the country. The official returns of foreign trade show an increase both in imports and exports, but here, too, there are indications pointing to the beginning of an accumulation of imported merchandise. In the year 1911 the imports have for the first time exceeded the exports, the balance representing a value of nearly \$ 10 000 000. The crop-prospects are said to be favourable, whereas it is known that last year's harvest, owing to drought, was not a good one. Still, after a series of favourable harvests such as has occurred in Chili, this single failure of crops does not signify very much. The condition of the national finances, however, remains unfavourable. Internal and external debt, paper money and railway-guarantees have, it is said, piled up a National Debt of 1000 million Pesos paper, representing over 300 Pesos paper per head of the population, a figure equalled in no other country. It is to be desired that ways and means will be found to take up with some energy the paying-off of foreign loans, for this is the only way of putting an end to the instability of the rate of exchange, which is such a serious obstacle to the economic progress of Chili.

It is to be regretted that in Peru no change for the better can be discerned. It is true that agriculture continues to develop favourably and that cotton, sugar and rice have realized profitable prices, but the greater part of the natural wealth of the country is still awaiting rational exploitation. We understand that much is expected for Peru from the opening of the Panamá Canal, and that it is believed that, when this has been accomplished, North American enterprise will turn towards the country. It is to be hoped that these dreams may be realized, but we doubt whether, for some years to come, much can be expected from the purchasing

power of this market, where at present the consumption of articles of our branch of industry is very moderate.

Japan has once more been favoured by excellent rice- and silk-crops and experience shows that a satisfactory consequence of such a result is an increased demand for articles of luxury by all classes of the population. Business in our branch, which, owing to the necessity of the people to practise economy, as explained in our last October Report, had been quiet throughout the first half of the year, was just beginning to revive in the autumn when suddenly the outbreak of the revolution in China put an end to all hopes. As a large proportion of our goods is worked up in Japan for subsequent export to China, it is not surprising that the state of insecurity of the latter country, which is such an important selling-market for Japanese products, at once brought about a restriction of business with the former. The demand for the Japanese home-trade has been satisfactory. High expectations are entertained in Japan of the Sayonji-Ministry, which has now been in power for some months and is apparently imbued with an earnest desire to place the finances of the country upon a more healthy footing. Similar endeavours by the Katsura Government were failures. The Marquis Katsura himself, as an old soldier, was unable or unwilling to place some curb upon his eagerness for a further increase in the Navy and the Army, and his financial reform-schemes were therefore doomed to failure. In the Budget recently brought in by the Minister of Finance, Yamamoto, the new credits for the fighting services have been restricted to a minimum. If the new Government should be long-lived, there is ground for hoping that there will be a thoroughgoing improvement in the national finances, with a consequent increase in the purchasing power of the people.

Of the foreign trade of Japan in the year 1911 the *Deutsche Export-Revue* gives the following particulars: "The total value of the external trade of Japan in the past year exceeded 1018 million yen, being made up as follows (in 1000 yen): Exports 488602 (against 472552 in 1910), imports 529222 (against 472347 in 1910); to which must be added bullion exports 29349 (25521) and imports 24385 (22659). Although the figures for 1911 constitute a record, the Japanese export returns were nevertheless not quite satisfactory, as the great expectations that were entertained at the beginning of the year did not come to fruition. This was due in the first place to the outbreak of the Chinese revolution, which lamed trade with that country for the time being. The imports showed a considerable increase, partly the result of the coming into force of the new Customs Tariff in July of last year, and partly owing to the considerable importation of rice consequent upon the failure of the previous year's (1910) rice-crop in Japan."

As regards China, we have but little to report, and that little is unsatisfactory. The heavy wounds inflicted upon all parts of the country

by the revolution are only too familiar ground, and it need scarcely be stated that while everything is at sixes and sevens all business-intercourse with this great market is suffering heavily. A considerable time must elapse before the new form of Government can inspire confidence, and before a return of peace and security will permit of the revival of trade and traffic from their present prostrate condition.

Commercial Notes and Scientific Information on Essential Oils.

Oil of *Acronychia laurifolia*, Bl. At Buitenzorg¹⁾ 198 kilos leaves of this laurel, known in Java as *kisarira*, yielded 133 cc. oil, possessing the following constants: $d_{20} 0,915$, $\alpha_D + 1^\circ 52'$, sap. v. 11, ester v. after acet. 50,9. The oil contained no aldehydes.

Almond Oil, pressed, from Almonds (German Pharmacopœia V). The hope of lower prices which we expressed in our last Report has unfortunately not been fulfilled, for throughout the winter months the appearance of both the Apulian and the Sicilian almond markets has been very firm indeed. In spite of the high prices the product of last year's crop found ready buyers, and at present only small stocks are left, for which 208 *M* per 100 kilos is asked. The available reports with regard to the present state of the flowers are favourable, but the danger of frost will not be past until after the next four weeks, and it would therefore be premature at this stage to describe the coming crop as in all probability likely to be a good one. The prices of almonds of the new crop for future delivery, which are at present entirely speculative, have fallen by a few marks as a result of the prospects. During the winter the sale of our own expressed almond oil has been normal, and there was no difficulty in obtaining the unaltered high prices. As already stated the remaining stocks of sweet almonds are small, and doubtless therefore the present value will be maintained until the summer.

Almond Oil, pressed, from Apricot kernels. The forecast in our last Report of the probable course of the apricot-kernel market has on the whole been fulfilled. The deficiency in the Californian crop prevented a further fall in prices, which otherwise would probably have followed upon the favourable crop in the district of Damascus, and the quotations, with few fluctuations, remained at about 69 *M* per 100 kilos. After the outbreak of the war between Italy and Turkey some depression had been

¹⁾ Jaarb. dep. landb. in Ned.-Indië, Batavia 1910, 49.

expected, Italy being an important consuming market of apricot kernels and commercial intercourse between the two countries having ceased entirely owing to the enormous war-duties imposed by the Customs of each nation upon the products of the other. But it would seem that Italy had covered her principal requirements before the outbreak of the war. In Hamburg the demand has left somewhat to be desired; in that market attention has been paid to Japanese and Chinese kernels, which were obtainable more cheaply than Damascene kernels, at any rate temporarily. It will be remembered that we had already revised our prices for expressed almond oil from apricot kernels in the previous autumn, in order to bring them into accord with the new market value of the 1911 crop; hence our quotations could remain unaltered. The demand has been normal, and so has that for genuine essential bitter-almond oil, although, since the incorporation into the Pharmacopœias of artificial chlorine-free bitter almond oil, and the consequent admission of that product in the manufacture of articles for human consumption, the cheaper artificial oil is of course preferred in many quarters. There is, however, a not unimportant difference between the two oils in respect of taste, and this is often disregarded by the manufacturers who employ these oils. It may be added, however, that manufacturers who have formerly been in the habit of using "very cheap" bitter almond oils, free from hydrocyanic acid, with a "guarantee of genuineness", are obviously unlikely to notice much difference when employing artificial oil.

G. Bertrand and A. Compton¹⁾, who have recently been engaged in investigations on the influence of temperature upon the activity of emulsin, have discovered that at a raised temperature the constituents of emulsin, amygdalinase and amygdalase, affect amygdalin almost equally. In the course of an experiment extending over 15 hours the maximum action of the enzymes upon amygdalin is attained at about $+40^{\circ}$; in a two hours' experiment at about $+56^{\circ}$ for amygdalase, and at about $+58^{\circ}$ for amygdalinase.

Ambrette Seed Oil. The price of ambrette seed has risen by more than 100 per cent. in the course of the last twelvemonth, and the only reason why ambrette seed oil maintained its previous cheap price for some considerable time was the existence of fairly large stocks both of seed and of oil. These have now been cleared off, and our quotations have followed the market-value. It is now a considerable time since supplies have come to hand from the various countries of production, and for the present orders for the raw material can only be placed at prices which must be described as exorbitant.

¹⁾ Bull. Soc. chim. IV. 9 (1911), 71.

Up to the present little is known of the properties of the valuable oil of ambrette seed, for which reason we record below, as a matter of general interest, the limits of the constants of our own distillates prepared in the course of the last few years, as determined by us. It is well-known that the normal distillate of ambrette seed is of a wax-like consistency, due to the large proportion of high-molecular fatty acids (palmitic acid) which it contains, and that the liquid oil, from which all odourless admixtures have been removed, is obtainable only by special treatment.

1. Normal, solid distillate:

d_{400}	acid v.	ester v.	sol. pt.	
0,891	75	66	38	} insol. in 10 vols. 90% alcohol.
to	to	to	to	
0,892	132	113	39°	

A product melting at about 47° gave d_{500} 0,8834 and was soluble in about twice its vol. and more 90% alcohol.

2. Liquid Oil:

d_{150}	α_D	n_{D20}	acid v.	ester v.	
0,9088	+ 0° 14'	1,47421	0	167,7	} sol. in 3 to 6 vols. a. m. 80% alcohol.
to	to	to	to	to	
0,9123	+ 1° 19'	1,47646	2,4	180,5	

Oil of *Andropogon intermedius*¹⁾. This species of *Andropogon* (comp. Report April 1909, 18) contains, as ascertained at Buitenzorg¹⁾, only 0,03% oil: d_{260} 0,919, α_D — 15° 30'. *Andropogon odoratus*²⁾ yielded 0,35% oil (d_{260} 0,914; α_D — 31° 10'), while the distillation of *Andropogon procerus* (?) only afforded 0,08% oil.

Angelica Oils. The scanty quantity of oil produced as the result of last autumn's distilling-season has of course maintained its exceptionally high level of prices throughout the winter, and it was only the approaching spring which induced several manufacturers somewhat to moderate their demands. We have followed this decline in our own quotations. In our opinion there is no cause for anticipating that the result of the present year's crop will be specially favourable, seeing that young plants are wanting everywhere, the 1911 sowings, both here at Miltitz and in Thuringia, having been a total failure owing to drought. It is therefore probable that the market conditions will shape themselves practically the same as last year, and consumers will be well-advised if they cover their requirements for the present year at the prices now current, which are in our view only transitory. The unfavourable conditions prevailing in angelica

¹⁾ The author-names are not stated in the original; we suppose that *Andropogon intermedius*, R. Br. and *A. odoratus*, Lisb. are meant. The latter was referred to in our Report of April 1907, p. 36.

²⁾ Jaarb. dep. landb. in Ned.-Indië, Batavia 1910, 48, 49.

root oil also apply to angelica seed oil. Our moderate stocks have been exhausted and for the present, therefore, we are compelled to refuse orders of importance, such as come to hand from time to time, especially from England. We only expect a small yield next autumn from our own plantations, but possibly, before that time, we may by chance discover elsewhere a parcel of raw material for distilling.

Anise Oil, Russian. Already in our last Report we pointed out that the yield of the 1911-crop had fallen far below that of the previous year, and the advices which have since come to hand have unfortunately not only confirmed our statement, but have placed the fact of the complete failure of the crop beyond doubt. In well-informed quarters the total quantity harvested is estimated to have been 100000 Poods, as compared with 245000 Poods in the year 1910. At the close of the last fair at Alexeyewka, which, owing to the delayed supplies, could not be held until November 14, it was possible to obtain a general idea of the paucity of the yield. Qualitatively also, the anise brought to market was worse than had been expected, and for seed with a very poor oil-yield from 53 *M* to 55 *M* per 100 kilos cif. Hamburg was asked. In these circumstances it is hardly necessary to say that the distillers of anise in Russia were only able to manufacture sufficient for their barest necessities, especially because, with such prices as these for their raw material, it was impossible for them to compete successfully with pure anethol, in the manufacture of which, fortunately, anise seed can be dispensed with. The prices of pure Russian anise oil with high solidifying point (18°) at times approached as high a figure as 20 *M*, but this quotation could not be long maintained in view of the reserved attitude of the buyers. At the moment it would be possible to buy from first hand at about 17,75 *M* to 18 *M*, but in spite of this the market must be called exceedingly firm.

Apopin Oil, see Linaloe Oil, p. 92.

Arnica Oils. We have at our disposal a sufficiency of the finest arnica flower oil of our own distillation to last us until the summer; on the other hand there is still a complete lack of arnica root oil (an article which is in fairly strong demand in the cosmetics trade), because in spite of all our efforts we have been unable to discover any raw material for distilling purposes. The reports from all districts where arnica root is gathered agree in stating that no supplies of any sort have come to hand owing to the exceptional drought of last summer.

Oil of *Artemisia frigida*, Willd. ("Wild Sage"). The oil of this American Composita, which was described by Rabak¹⁾ some years ago has since then been more closely examined by him²⁾. The plant, which was

¹⁾ Comp. Report October 1905, 12; April 1907, 13.

²⁾ U. S. Dep. of Agriculture, Bureau of Plant Industry, Circular No. 235, p. 21.

collected in South Dakota, yielded 0,26% oil (calc. based upon green herb?), possessing the following constants: $d_{24^{\circ}}$ 0,940, α_D — 24,2°, $n_{D24^{\circ}}$ 1,4716, sol. in 1 vol. 80% alcohol, acid v. 2,5, ester v. 25, ester v. after acet. 139. When the oil was allowed to stand 3% *l*-borneol (m. p. 203°; $[\alpha]_D$ — 32°) separated out from it. Caprylic and α -nanthic acids were probably present in the free state, and α -nantic acid, valeric acid, with traces of formic and undecylic acids, in the esterified form. The oil further contained the following constituents: 18 to 20% cineole (m. p. of the iodol-compound 110 to 113°) and 8 to 10% *l*-fenchone (m. p. of the oxime 164 to 165°). The oil contains a total of 43% borneol, of which 35,6% is free borneol and 6,8% is in the form of α -nanthic ester.

Oil of *Artemisia lavandulæfolia* (?). A few years ago¹⁾, we referred under the name of *Artemisia lavandulæfolia* to a product distilled at Buitenzorg, which contained an unidentified solid body, possessing the molecular structure $C_{12}H_{14}O_2$. From a subsequent reference to this oil²⁾, we gather that it is most probably derived from another plant than that named above, but so far it had been impossible to procure a fresh supply of raw material to elucidate the botanical origin. The solid body is precipitated in the oil when light petroleum is added. It has m. p. 32,5 to 33°, contains a methoxyl-group and absorbs 3 molecules bromine. The body was heated for a few hours with potash liquor, consuming 2 molecules potassium hydroxide. The reaction-product was then treated with steam, when a body with an odour of amylacetate passed over. This was possibly methyl heptenone. With iodine and potash liquor the distillate gave a pronounced iodoform reaction. After acidulation, *n*-butyric acid distilled over. The solid body probably represents the methylester of an unstable acid.

Asafoetida Oil. In a paper on the detection of galbanum and ammoniacum in asafoetida, H. M. Sechler and M. Becker³⁾ state, *inter alia*, that such an admixture is also observable in the essential oil obtained from the resin in question. While pure asafoetida is said to yield a colourless oil⁴⁾, asafoetida adulterated with galbanum or ammoniacum yields a more or less yellow-coloured distillate. It is stated that an addition to asafoetida of as little as 10% of the gum-resins referred to may be detected by this test.

It is further asserted that the refractive index also affords a guide to the possible adulteration of asafoetida with galbanum or ammoniacum, the refraction of the last-named resins being lower than that of asafoetida. Sechler and Becker regard an asafoetida oil with a coefficient of refraction

¹⁾ Report April 1909, 20.

²⁾ Jaarb. dep. landb. in Ned.-Indië, Batavia 1910, 45.

³⁾ Americ. Journ. Pharm. 84 (1912), 4.

⁴⁾ Gildemeister and Hoffmann, in *The Volatile Oils* (p. 574), stated that the colour of asafoetida oil varies from yellow to brown.

below 1,4960 (25°) as suspect, an assumption which seems to be very much in need of corroboration, and which, for instance, is not in accord with the statements by E. F. Harrison and P. A. W. Self set forth below.

Harrison and Self¹⁾ have also investigated asafoetida and have presented the results of their observations in a paper read before the Pharmaceutical Society of Great Britain. They examined 15 different samples of asafoetida, drawn from large parcels. They determined the percentages of loss on drying in a water-oven, the percentage of resin, of mineral constituents (ash) and of essential oil. The latter they examined more closely. With the exception of one sample, which came from Bombay, all the samples had been taken from parcels imported from the Persian Gulf. We will here only refer to that part of the interesting paper which deals with the examination of the essential oil.

Harrison and Self determined the oil-content of each sample by steam-distillation. By this method they obtained from 5,8 to 17,1% oil, that is to say, in part considerably higher yields than had been observed previously²⁾. Umney and Bunker³⁾ alone have obtained approximately equal values (from 12 to 16%) but these were obtained by a different method of determination.

The characters of the oils obtained from Persian asafoetida fell within the following limits of value: $d_{15,50}$ 0,915 to 0,981, $\alpha_D + 9^\circ 39'$ to $-17^\circ 3'$, n_{D20} 1,4942 to 1,5207. Sulphur-content 17,5 to 29,2%. A high sulphur content was mostly found in combination with high sp. gr., high refraction, and dextrorotation.

The gum-resin from Bombay yielded 7,5% oil of somewhat different constants ($d_{15,50}$ 0,993; $\alpha_D - 35^\circ 55'$; n_{D20} 1,5250; 37,8% sulphur) and, according to Harrison and Self, is probably less valuable than the other samples.

The experience of Umney and Bunker (*loc. cit.*) that oil from asafoetida in tears contains a higher proportion of sulphur than oil from asafoetida in mass has not been confirmed by Harrison and Self; on the contrary, their samples showed the same average sulphur-content, whether mass or tears. They believe that Umney and Bunker have operated under serious loss of sulphur, volatile sulphur-compounds having escaped in the course of their examination. They themselves have tried to determine the sulphur-content by different methods and have come to the conclusion that the following method is that which yields the best results:—

About 0,5 g. of the oil is weighed into a 150 cc. flask, connected by a ground joint to the tube of a vertical condenser; 5 cc. of water is added through the tube, followed by 5 cc. of nitric acid ($d_{15,50}$ 1,42). The flask

1) Pharmaceutical Journ. 88 (1912), 205.

2) Gildemeister and Hoffmann (*loc. cit.*) give from 3 to 6,7%

3) Comp. Report October 1910, 20.

is warmed, if necessary to start the action, which then proceeds somewhat vigorously. Next 3 g. of powdered potassium bromide is dropped in through the condenser tube, the liquid boiled for ten minutes, cooled, and 5 g. of caustic soda, dissolved in a little water, added in the same manner. The liquid is then evaporated to dryness in a platinum vessel and ignited. The residue is dissolved in water, nitric and nitrous acid removed by evaporation with hydrochloric acid, and the sulphate determined in the usual way.

According to Harrison and Self the best evidence of the value of asofoetida is to calculate the sulphur-content of the oil for the drug after deducting the ash. Present experience shows that the oil of the genuine drug does not contain less than 1,5% of sulphur.

Oil of Sweet Basil. This article continues to suffer from lack of enquiry, and as a result there has been some accumulation of stock. Offers of considerable quantities from some of the producing centres appear to show that the distillation of the oil has again been taken up somewhat more assiduously than formerly. We must, however, earnestly caution the producers against indulging in too optimistic anticipations of the future of this article, for its consumption has decidedly decreased, and even at a heavy sacrifice it would be very difficult to dispose of large quantities.

Bay Oil. The scarcity which we have had to chronicle for several years past still continues, and the small arrivals which have come to hand from time to time at Hâvre, Marseilles and Hamburg have always found ready takers. Occasionally the supplies consisted of oil which had been adulterated almost out of recognition, and scarcely deserved the name of bay oil. Judging by the most recent advices the present conditions of the market are likely to continue for some considerable time, inasmuch as the native producers in the West Indian Islands have again begun to complain that it is difficult to procure sufficient quantities of leaves. In any case there is not the slightest prospect of our being able to resume distilling operations here, which we regret the more because none of the parcels of West Indian oil which have thus far come into our possession even distantly approaches in quality our own distillate. We must limit ourselves to the exercise of the greatest possible care in selection from among the supplies of oil which come to market, but in doing so we are not always able to satisfy all our customers' requirements in the matter of prices, for it goes without saying that we ourselves have to pay proportionately high rates for the finer qualities. In spite of the considerable increase in price which we have been compelled to make, our exquisite terpeneless bay oil continues to be in strong demand, which proves that the high value of this product is justified by its excellence.

Bayberry Oil. An oil distilled by F. Rabak¹⁾ from the leaves and twigs of *Myrica cerifera*, L. (N. O. Myricaceæ) gave the following constants: $d_{20} 0,9168$, $[\alpha]_D - 1,5^\circ$, $n_{D25} 1,4945$, acid v. 3,5, ester v. 21, sap. v. after acet. 58. The oil was soluble in one-half its own vol. of 90% alcohol, the solution becoming turbid upon the addition of 2 vols. or more; it was insoluble in 80% alcohol. The yield was 0,015% (calc. based upon green herb?).

Rabak describes the oil as a novelty, but this is not quite correct, the distillate having been mentioned by Hambricht²⁾ as long ago as the year 1863 and having been described by us in our Report of October 1894, p. 70.

Birch Bud Oil. A few weeks ago we were successful in procuring in Russia a fine parcel of birch buds, the distillation of which has enabled us to make a corresponding reduction in our prices. We strongly urge the larger consumers to secure a quantity for delivery as required, experience having shown that it is very often difficult to procure supplies of raw material.

Buchu Leaf Oil. Unfortunately there has been no change in the position of this article. We have not yet succeeded in replenishing our stocks, for we have been unable to discover raw material suitable for distilling. The demand, it is true, has been very slight, so that the lack of supplies has not been particularly severely felt.

Oil of Bupleurum fruticosum. L. Francesconi and G. Sanna³⁾ have discovered that the oil of this umbellifer⁴⁾, in addition to an alcohol and an ether of unknown character, contains a large proportion of a terpene possessing the following characters: b. p. 167 to 169°, $d_{14} 0,8416$, $\alpha_{D17} + 35,7^\circ$, $n 1,4862$. It polymerises into a white, amorphous mass, m. p. 90 to 100° ($[\alpha]_D - 66,14^\circ$).

The same authors, in another paper, which has been published in the *Atti R. Accad. dei Lincei, Roma* (5), **20**, II. (1911), p. 190⁵⁾, describe the action of nitrosyl chloride upon the essential oil. They dissolved 5 cc. of the oil in 20 cc. alcohol, admixed thereto 7 cc. amyl nitrite or 11 cc. ethyl nitrite and diluted with 8,5 to 9 cc. alcohol which had been saturated with hydrogen chloride. Treated by this method, the various fractions always yielded the same nitrosochloride, whereas Wallach's method gave no result. The nitrosochloride probably represents a mixture; it melts between 80 and 97°, chiefly between 92 and 94°; $[\alpha]_D - 196,2$ to $-210,6^\circ$. By dissolving

1) Midland Drugg. and pharm. Review **45** (1911), 484.

2) Americ. Journ. Pharm. **35** (1863), 193.

3) Gazz. chim. ital. **41** (1911), I. 796. Copies of this paper, and of those mentioned in the succeeding paragraphs, were kindly sent to us by the authors. Quoted from Chem. Zentralbl. **1911**, II. 1450.

4) Comp. Report October **1911**, 23.

5) Quoted from Chem. Zentralbl. **1911**, II. 1805.

in chloroform and precipitating with methyl alcohol it can be split up into a less soluble portion, m. p. 100 to 101° ($[\alpha]_D - 285^\circ$), and a more readily soluble portion, m. p. 101 to 102° ($[\alpha]_D - 175^\circ$). From the nitrosochloride Francesconi and Sernagiotto¹⁾ obtained dihydrocuminic aldehyde.

By eliminating nitrosylchloride from the nitrosochloride the authors obtained *d*- β -phellandrene ($[\alpha]_D + 19,65$ to $53,32^\circ$). Whether the oil also contains α -phellandrene is very doubtful. The authors²⁾ prepared the dihydrocuminic aldehyde by prolonged boiling of the nitrosochloride with a mixture of 3 parts water and 10 parts acetic acid. Its characters are as follow: b. p. 136 to 140° (15 mm.), $d_{15} 0,9825$, $n_{15} 1,528$. The semicarbazone melts between 197 and 198°. When oxidised with oxide of silver in alcoholic solution it forms cuminic acid (m. p. 116 to 117°).

From the phyto-physiological standpoint, the investigations of Francesconi and Sernagiotto³⁾ into the localisation and distribution of the essential oil in the *Bupleurum* plant are also interesting. The younger the leaves, the greater their essential-oil content. The presence of oil may be detected not only by extraction but also microscopically by means of osmic acid, "Soudan III" (aminoazobenzolazo- β -naphthol) or Mesnard's reagent.

The authors⁴⁾ give the following particulars of the oil-yield: the branches of plants distilled at Laconi (prov. of Cagliari) contained 1% oil; the leaves, during the flowering period, yielded from 1 to 3%, and the flowers distilled separately, 3,75% oil. The calculation of the yields appears to be based upon the green herb.

Cajuput Oil. Business in this article has taken a somewhat more animated turn within the past six months, and as a result the export figures up to the end of November, which are the latest available, show an advance as compared with those of the corresponding period of last year. The shipments were as follows:—

1911	1862 baskets
1910 :	1536 „
1909	1309 „

As mentioned in our last Report, the total exports for the year 1910 amounted to 1739 baskets, that is to say considerably less than the shipments of the first eleven months of 1911.

¹⁾ Atti R. Accad. dei Lincei, Roma (5), 20 (1911), II. 325. Quoted from Chem. Zentralbl. 1912, I. 345.

²⁾ Atti R. Accad. dei Lincei, Roma (5), 20 (1911), II. 388. Quoted from Chem. Zentralbl. 1912, I. 345.

³⁾ Atti R. Accad. dei Lincei, Roma (5), 20 (1911), II. 111. Quoted from Chem. Zentralbl. 1911, II. 1540.

⁴⁾ Atti R. Accad. dei Lincei, Roma (5), 20 (1911), II. 230. Quoted from Chem. Zentralbl. 1911, II. 1805.

We have again received, quite lately, considerable parcels of this oil from our reliable source of supply in the island of Buru, and these are not included in the figures given above.

The prices have been subject to slight fluctuations only and, generally speaking, have maintained their present level.

Calamus Oil. In directing attention to our superior distillate, we do so with the more emphasis because just lately we have been asked to give an opinion on oil-samples from competing quarters which, although normal as regards their constants, possessed such a peculiar aroma that their employment in, say, the manufacture of liqueurs, must be attended with serious and costly disappointments. For this reason we would earnestly point out to those who are interested in the article, and especially to the distributors, that in purchasing calamus oil it is quite a mistake to regard the question of price as of prime importance.

Camphor Oil. On the whole the position of this important oil may be described as unaltered. Considerable stocks of cheap crude oil still exist both in Europe and in the United States, and for that reason the selling prices have not as yet reflected the increased rates which have had to be paid to the Japanese for the most recent purchases. Both light and heavy camphor oil have been in brisk demand; considerable quantities have changed hands, and the weakness in the turpentine oil market has by no means been able to hamper the trade in camphor oil. Generally speaking the position of the article must be called very firm, for the Japanese refuse altogether even to consider counter-offers to their demands and they are very cleverly taking care to place upon the market only just enough of the different varieties of crude oil to supply the demand for the time being, and above all to prevent an over-supply.

In our Report of April 1911, p. 31, we stated that a Mr. Anderson, an American interested in the camphor trade, had lodged a protest with the Japanese authorities against certain alleged irregularities practised in that trade. In view of the antagonistic interests of the Japanese and the foreign camphor-refiners, Mr. Anderson has come to the conclusion that the only means of saving the camphor trade is the creation of a Trust embracing the Japanese and the American manufacturers, and also, if possible, the British, German, and French importers. He has explained his views to the leading interests in Japan and in the United States, but it is considered doubtful whether it will be possible to secure the co-operation of the parties in Europe who are interested in the trade, although there may be no difficulty in bringing "under one hat" the Japanese and the American manufacturers. It is said that the Japanese firms have

¹) Chem. Zeitschr. 10 (1911), 210.

made it a condition that the Trust shall buy from them 12 000 000 lbs. of camphor annually.

According to a British Consular Report¹⁾ the Japanese camphor refiners, at the beginning of last year, complained to their Government of being compelled to pay 5.80 yen per 100 kin more their camphor than was charged to their competitors in Europe and America, whereupon the Monopoly Bureau raised the price of the "BB" brand of camphor from £ 7.5/- to £ 7.10/-. The total production of camphor in Japan in the year 1910 remained below the estimated figure of 7706000 lbs.; the experiments for preparing camphor from the leaves are as yet (still?) in the initial stage. The forests in Southern Formosa, which have been principally exploited up to the present, yield a product which often contains 400 parts of oil to 100 parts of camphor, while the product of the Northern forests, which have recently been secured by force of arms from the attacks of the aborigines, only yields 75 parts of oil to 100 parts of camphor. For this reason it is probable that the year 1911 will already show a considerable increase in the camphor-production of Formosa.

From the XIth Financial and Economic Year-Book for Japan we quote (through a trade report) the following particulars concerning the production and export of camphor in Japan and Formosa²⁾.

In Old Japan the output of crude camphor from 1931 distilling-plants amounted to 1354454 kin, representing a value of 798489 yen. The exports in the year 1910 (whether of crude camphor only or of crude camphor and camphor refined in Japan is not clear), represented the following values:

To British India	477 649 Yen
„ France	748 626 „
„ Germany	322 430 „
„ United Kingdom	580 023 „
„ U. S. A.	691 029 „
„ Other countries	144 612 „
	2964369 Yen

In connection with the above it should be stated that the great fluctuations in the exports to France, Germany and the United Kingdom are explained by the fact that the individual cargoes are usually shipped under option London, Hâvre, or Hamburg, and that in every case the first port touched by the steamer carrying the freight is regarded as the place of export for statistical purposes.

The production of camphor in Formosa has remained fairly stable in recent years, whereas the value of the exports shows considerable fluctuations: —

¹⁾ Chem. Zeitschr. **11** (1912), 5; also comp. Report October **1911**, 25.

²⁾ Comp. our previous communications, Report April **1911**, 32 *et seq.*

	Production	Value of Exports
1907	3914598 Kin	2619143 Yen
1908	3534970 "	1710493 "
1909	3537712 "	4377816 "
1910	4864704 „ ¹⁾	4932750 "

According to B. A. Bond it is estimated that the camphor forests of Formosa will be exhausted in 45 years' time, but since 1901 the Japanese Government has caused 15000000 young trees to be planted.

According to a U. S. A. Consular Report²⁾ from Tamsui in Formosa, the camphor exports from that island during the first eleven months of the year 1911 amounted to 4788270 lbs., value \$ 1486934. This represents a decline in value of \$ 100000 in round figures as compared with the corresponding period of the previous year. This reduction is chiefly accounted for by a falling-off in the exports to the U. S. A., but the shipments to Germany and France are also said to have declined. According to a report received at the Bureau of Labour of the U. S.³⁾ a similar reduction is shown in the export-figures relating to Chinese camphor from the port of Foochow, which fell from 524800 lbs. in the year 1909 to 130800 lbs. in the year 1910. The principal refinery, which was carried on by a British firm, has closed down, and only one refinery still keeps going. Crude camphor is scarce, and from the forests in the interior no increased supplies are to be expected.

In our Report of April 1911 we called attention (p. 36) to the decrease which was taking place in the exports of camphor from China. We give below the statistics of the exports from the ports of Shanghai, Amoy, and Foochow, taken from a French journal⁴⁾: —

Export in Piculs	1907	1908	1909	1910
Via Shanghai	4 607	4 064	4 889	4 410
Via Amoy and Foochow	19 711	8 257	3 945	1 005

In our last Report (p. 27) we referred to a statement by Hutchins on the occurrence of camphor-trees in German East Africa. Hutchins declared in his article that neither the botanists of the Imperial German Biological-Agricultural Institute at Amani, nor the forest officials at Wilhelmstal had recognised the tree. This statement, we are informed by Prof. Zimmerman, Director of the Institute in question, is incorrect; on the contrary, the tree was perfectly well known to the officials at Amani by the name of *Ocotea*

¹⁾ Comp. Report October 1911, 25.

²⁾ Oil, Paint and Drug Reporter 81 (1911), No. 1, p. 28F.

³⁾ *Ibidem*, p. 40.

⁴⁾ Journ. d'Agriculture tropicale 11 (1911), 319.

usambarensis, Engl. An oil prepared from its bark at Amani was examined and described many years ago by Schmidt and Weilinger¹⁾. The bark has also been tested for tanning-materials, but it is said to contain only about 11% of the latter²⁾.

It is only now made known by a lengthy quotation in the *Bulletin of the Imperial Institute* [Vol. 9 (1911), 340] from a Report on the Forests of British East Africa, 1909, that Hutchins himself as long ago as 1909 had identified the tree which he describes as "Ibean Camphor tree", as *Ocotea usambarensis*, Engl. Nothing of this kind was stated in the abstract which served as the basis for the paragraph in our Report of October 1911.

Schmidt and Weilinger at the time only examined the oil from the bark of the tree, but the Imperial Institute had at its disposal a series of samples of the wood in the shape of sap-wood possessing a faint odour of eucalyptus oil; branches and twigs, which, when newly broken, also gave off the same odour, but in a more marked degree; and, lastly, pollard shoots which had sprung up from the stumps of felled trees after a few years' interval. Each of these three samples, when distilled with steam, yielded a volatile oil possessing the following properties: —

	Oil from			
	Sapwood	Branches and twigs	Branches and twigs (Pollard shoots)	Bark; Schmidt and Weilinger
Yield	0,4%	0,52%	0,14%	0,15%
d_{150}	0,9641	0,9681	0,9327	0,913 bei 20°
α_D	— 7° 30'	— 7° 30'	— 0° 28'	— 11° 12'
Sap. v.	30,1	30,1	13,3	13,7
Sol. in 80% alcohol	In 1,1 vols.	In 1,1 vols.	Insol. even in 10 vols.	—

The first two samples of oil were of a bright yellow colour and reminded of eucalyptus oil in their odour. They only contained comparatively little cineole, and no camphor could be detected in them. The oil from the shoots was of a thinner consistency than the other oils, but resembled them in odour and colour; its more powerful odour led to the conclusion that its cineole-content was greater, but the sample was too small to permit of a cineole-estimation.

In our Report of October 1910 (p. 27) we discussed a paper by Lommel on the preparation of camphor at Amani. A second paper by the same author³⁾ contains some interesting data on the distillation of dried camphor

¹⁾ Berl. Berichte 39 (1906), 652; Report April 1906, 68.

²⁾ Der Pflanze, Ratgeber f. trop. Landwirtschaft 4 (1908), 222.

³⁾ Der Pflanze, Zeitschr. f. Land- und Forstwirtschaft in Deutsch-Ostafrika 7 (1911), 441.

leaves, of which a synopsis is given below: The author first deals with the distillation of leaves which had been spread out for drying in a small cinchona-plantation shortly before the setting-in of the rains, but which were not yet quite dry. The camphor-yield from these leaves was too small to make it worth while estimating it, and the experiment was set down as a failure. For a subsequent distilling-experiment a plantation was subjected to moderate cutting, when a quantity of dry fallen leaves was found on the ground between the rows of plants. These were first distilled and only yielded 0,06% crude camphor and 0,19% camphor oil, showing that they had lost almost the whole of their volatile constituents during the long time they had been lying on the ground drying, exposed to the alternating effects of rain and sun.

Next the green leaves were dried on previously cleaned ground under the shade of cultivated cinchona trees. In the course of about a fortnight they were dry enough to be readily stripped from the branches and, collected in sacks, they were carried to the still. This experiment gave a thoroughly satisfactory result, the yield being 1,55% crude camphor and 0,49% camphor oil. The result would certainly have been better still but that on one occasion, in the course of the distilling process, the condensing-water became heated, and a not inconsiderable quantity of camphor was thereby lost.

In view of the fact that present experience on the effects of cutting upon the growth of the trees shows it to be a pretty well established fact that it is possible to cut the trees twice a year, it is reasonable to expect a five-year old plantation to yield about 8400 lbs. of dry leaves per acre. This would be equivalent to an output per acre of about 325 lbs. of camphor and about 103 lbs. of camphor oil.

H. W. Emerson and E. R. Weidlein¹⁾ have distilled camphor oil in Jamaica, and have confirmed the observation recently made that the leaves of the plant can be successfully employed for this purpose. From 56,940 kilos green leaves they obtained 1353,8 grams = 2,35% crude camphor and oil (1,32% camphor, 0,54% camphor oil and 0,49% water), and from 67 kilos dry leaves 1719,5 grams = 2,54% of a distillate comprising 1,57% camphor, 0,46% camphor oil and 0,51% water; 22425 grams twigs and green leaves yielded 0,58% camphor and 0,26% camphor oil, 8770 grams twigs and dried leaves contained 0,54% camphor, and 1800 grams wood, when distilled, yielded 0,61% camphor.

Besides camphor the oil contained pinene, phellandrene, cineole, dipentene, and safrol. It is not quite clear from the reference whether the safrol was detected by the authors in oil distilled from the leaves or

¹⁾ Journ. Ind. Eng. Chem. 4 (1912); 33. Quoted from Journ. Soc. chem. Industry 81 (1912), 149.

from the wood, nor do we find any particulars showing how the constituents were identified.

From an article by H. Morstatt¹⁾ on insect pests in camphor-trees we quote the following: "Although camphor, which occurs in all parts of the camphor-tree, is itself an efficient protective against the attacks of insects, it is powerless to protect the parent-tree from such pests. Thus, in German East Africa the camphor-tree is attacked by slugs, shield-lice, locusts, bugs, mites and certain kinds of beetles. The weevil, *Dicasticus Gerstæckeri*, Faust is occasionally found in the tree in enormous numbers, and the capricorn-beetle, *Tragocephala pretiosa*, Hintz, an insect measuring from 8 to 10 inches in length, often inflicts serious damage upon the tree".

Cananga Oil. The upward movement in prices which all the producers agree in forecasting still tarries by the way, but this notwithstanding, and in spite of the fact that the arrivals continue to be sufficient for the demand, the position of the article must be described as steadily firm. We have lately made special arrangements for securing a sufficient future supply, and in all probability our customers will therefore be secured against unpleasant surprises. In any case, however, we consider it very desirable that consumers should secure their requirements for some months ahead at the present prices, for we regard a reduction in values as quite out of the question, and an upward movement must sooner or later make itself felt when the present important second-hand stocks are beginning to be used up, and if the producers should somewhat restrict their shipments, a contingency which appears to be extremely probable in view of the exceptional quietness of the market during the past few months.

"Cape" Oil. On the Ivory Coast the name of *Cape* is given to a particular kind of leaves²⁾ which are apparently used by the native women for perfuming their persons. Roure-Bertrand Fils have distilled the dry leaves, and obtained therefrom 0,28% of an extremely mobile, greenish-yellow oil of an extraordinarily powerful, agreeable odour, at first reminding of patchouly. The distillate gave the following constants: d_{150} 0,977, $\alpha_D + 39^{\circ}38'$, acid v. 0,7, sap. v. 109,2. It was soluble in its own volume of 80% alcohol, the mixture showing a slight cloudiness when more alcohol was added.

Caraway Oil. Throughout the winter no change has been perceptible in the caraway market, but if anything the prices, as a result of the exceptionally heavy crop of last year, showed a certain dulness. Recently, however, the position has undergone a change, inasmuch as the severe winter is reported to have seriously damaged the plantations. The caraway-fields, it will be remembered, had already suffered from last year's great

¹⁾ Der Pflanze, Zeitschr. f. Land- u. Forstwissenschaft in Deutsch-Ostafrika 8 (1912), 18.

²⁾ Berichte von Roure-Bertrand Fils, October 1911, 43.

heat, and one-half of the area then newly-sown has had to be ploughed up. It is certain that this circumstance will bring about a material shortage in the production, but it must be borne in mind that there is still a considerable balance in reserve from 1911, which, unless bought up by speculators, will help to average the market. In the meantime the prices which, as is well-known, had dropped to the neighbourhood of fl. 11, have advanced to about fl. 15,50, and a few parcels of new crop seed for delivery next September have even changed hands at fl. 17,50. It is obvious that these facts cannot remain without influence upon the prices of caraway oil, but generally speaking we regard the reports as very premature and we are of opinion that there is still ample time for changes in the position. This, however, is certain, that there will be no return to the exceptionally low prices which resulted from last year's abnormally heavy crop.

The above is confirmed by the recently-published report of the Dutch Ministry of Agriculture, which states: —

"The dry summer of 1911 has been very unfavorable to the caraway-plants. When the covering-crop was removed, the condition of the caraway-fields proved to be so bad that most of them were ploughed up. In all the important districts, such as Groningen, North-Holland, South-Holland, Zealand and Western North-Brabant, only a small section of the fields is under caraway. Thus, the State Instructor in Agriculture for Western North-Brabant estimates the area under caraway in his district at only from 10 to 20% of that of last year. The few caraway-areas which are in existence in Groningen at present date from last year. Moreover, the condition of the growing crop is not very satisfactory. In Groningen it is moderate to fairly good; in North-Holland, moderate on clay and fairly good on peat-soil; in South-Holland and Zealand moderate, and in North-Brabant bad."

Cardamom Oil, Ceylon. It has been necessary to raise the prices very materially, as all varieties of cardamoms suitable for distilling were almost unprocurable. The prospects are still very unfavourable and continued high values appear to be certain.

Cardamom Oil, East African, see p. 136.

Oil of *Casimiroa edulis*. Power and Callan¹⁾ have obtained from the alcoholic extract of the seeds of *Casimiroa edulis*, La Llave (N. O. Rutaceæ), a yield of 0,021% (calc. based upon dry seed) of an essential oil possessing the following constants: $d_{20} 0,9574$, $\alpha_D - 2^{\circ}25'$ (in a 25 mm. tube). The bulk of the oil boiled below 130° (25 mm.).

Cassia Oil. The cassia oil market calls for very little remark on the present occasion. It is true that shortly after our last October Report

¹⁾ Journ. chem. Soc. 99 (1911), 1996.

went to press the prices of 80–85% oil advanced to about 4/–, because the political troubles in China were not without their effect upon the article, but towards the end of the year the market quieted down again; the quotations receded to about 3/10, and at that figure they have since remained with slight fluctuations. On the whole the demand for cassia oil has been very quiet in all the markets which count in the determination of the price of the article; the consumers' requirements have been normal and the supplies regular, and the balance between offers and demands has been undisturbed.

Cassie Oil. In the *Philippine Journ. of Sc.* 6, A. (1911), 350, Brooks states that *Acacia Farnesiana*, (L.) Willd. has been imported into the Philippines and now occurs wild throughout the Archipelago. In his opinion it would be worth while cultivating the plant for the sake of utilising its flowers.

Cedarwood Oil. Under the heading "East African Cedarwood Oil" we referred on p. 105 of our last Report to the occurrence in East Africa of *Juniperus procera*, Hochst., a conifer which is of industrial importance in the manufacture of lead-pencils. *Juniperus barbadensis*, L. to which we find references in two different publications¹⁾ is closely related to the first-named species. It occurs in the pine-districts of Dominica, and also inhabits the other West Indian Islands, and the southern parts of North America. So far, no oil has been distilled from this plant. Besides the *Juniperus*-species mentioned above, *Pinus occidentalis*, S. W., and *Xanthoxylum martinicense*, Lam., occur in the pine-forests of Dominica.

On the oxidation of cedrene with ozone in acetic acid solution see p. 173.

Oil of Cedrela. F. Rabak²⁾ has distilled from the wood of *Cedrela odorata*, L. (N. O. Meliaceæ), a plant which occurs in the southern parts of North America, 0,3% of a golden-yellow essential oil with an odour of cedar. Its constants were as follow: d_{25}^0 0,947, n_{D25}^0 1,5038, acid v. 3,9, ester v. 41,5, ester v. after acet. 51; gives a cloudy solution with 6 vols. 80% alcohol.

Celery Oil. Following upon the complete failure of the celery-seed crop in France, to which we have already referred, it is not surprising that the prices of celery oil have undergone a proportionate advance. Our present selling-price is still comparatively low, inasmuch as it is based upon the cost of a few chance purchases we were able to secure, and at the current market-value of celery seed we should certainly have to pay higher rates for raw material. It is to be hoped that this year favourable weather will prevail and assure a normal crop of celery seed, for if this

¹⁾ Nachrichten f. Handel, Industrie und Landwirtschaft 1912, No. 1, p. 3; Kew. Bull. 1911, No. 9, 377.

²⁾ Midland Drugg. and pharm. Review 45 (1911), 486.

should not be the case it will be impossible to maintain the present price of celery oil, even if it should then be possible to procure any raw material at all for distilling.

Chamomile Oil, German. In the course of the winter we found an opportunity of procuring a few small parcels of raw material well-suited for distilling purposes, by which we were able to replenish our supplies so favourably that we were enabled slightly to reduce our prices. We are now in a position to quote special prices for important quantities and we shall be glad to receive enquiries where such quantities are in question.

Chamomile Oil, Roman. The small output of last season is practically exhausted, and those who have delayed covering their requirements until the new crop will be compelled to pay very high prices indeed, always assuming that they succeed in procuring a sufficient quantity at all. Our stocks have shrunk to within a very small compass and during the last few months we have been repeatedly obliged to advance our quotations.

Champaca Oils. B. T. Brooks¹⁾ has published an extensive paper on genuine champaca oil from yellow flowers (from *Michelia Champaca*, L.) an oil which has only lately been investigated by Bacon. The champaca trees which grow in the neighbourhood of Manila are rather smaller than the ylang-ylang trees. Their trunk has a diameter of from 8" to 20", while in the Botanical Gardens at Peradeniya in Ceylon there are specimens which measure from 3 to 6 feet in diameter. The trees are propagated from seed or from cuttings. The seed should be sown in sand to prevent it from rotting. In the year 1910 the trees flowered from the middle of June until the end of October, but this is exceptionally long, and was due to the comparative absence of rain during that period. The flowers must be worked up immediately after collection, as they contain a ferment which sets up an oxidising action, so that they turn brown in a short time and lose their pure odour. The oil²⁾ which was prepared by Brooks has the following constants: $d_{\frac{30}{30}^{\circ}}$ 0,904 to 0,9107, $n_{D\frac{30}{30}^{\circ}}$ 1,4640 to 1,4688, ester v. after acet. 199. It cannot be fractionated *in vacuo*, as it resinifies in the manipulation. Among the constituents of the oil Brooks found cineole (m. p. of the iodol compound 112 to 114°). It may also contain *p*-cresol-methylether, but it was impossible to establish the presence of this body. When the oil was shaken with sodium bisulphite solution benzaldehyde was isolated (m. p. of the phenylhydrazone 149 to 151°). It is probable that another aldehyde is present in addition to benzaldehyde but no further investigation was made on this point. As regards alcohols, Brooks detected benzyl alcohol, which he identified by oxidising into benz-

¹⁾ Philippine Journ. of Sc. 6, A. (1911), 333.

²⁾ The author does not state how he prepared the oil.

aldehyde. As regards acids, benzoic acid was found to be present in the saponification-liquor. The benzaldehyde-content of the oil is about 6⁰/₀, but it only contains 0,5⁰/₀ benzoic acid, and Brooks surmises that the last-named body is only formed by oxidation of the aldehyde or of the benzyl alcohol.

Champaca flowers contain a crystalline substance, for which Bacon sets up the empirical formula $C_{16}H_{20}O_5$. In contradistinction to Bacon's observations, Brooks found that this substance reacts quantitatively with bisulphite solution, but that it cannot be recovered from the bisulphite-compound. This peculiarity renders it not improbable that the group $CH:CH \cdot CO$ is present in this body¹⁾. The fact that the substance is a ketone is proved by its behaviour towards ammoniacal silver solution and magenta solution. The phenylhydrazone melts at 161°. The ketone does not react with acetanhydride, and with acetyl chloride it resinifies. When heated with an excess of alcoholic potash solution it gives rise to neutral succinate of potassium. It would seem that the succinic acid occurs in the ketone-molecule in the form of a neutral ester. In order to identify the alcohols which were associated with the succinic acid, the ketone was saponified with aqueous soda liquor, but only ethyl alcohol could be detected. Experiments at saponifying the body with soda liquor or with dilute acids were unsuccessful. It follows that one of the carboxyl-groups of the succinic acid is esterified with ethyl alcohol and the other with an alcohol $C_{10}H_{12}O_2$.

A communication by Brooks²⁾ to another journal contains in substance the same information as that abstracted above, but in addition we take from it the following particulars: in order to establish the existence of oxidase in the flowers, they were crushed below water. The process of crushing must be carried out under exclusion of air, by pouring a layer of paraffin oil upon the water, as otherwise the solution immediately assumes a brown colour. A yellow liquid is then formed, which gives the colour reactions with α -naphthol and *p*-phenylenediamine that are typical of oxidase. When the solution is heated on the water-bath the activity of the enzyme is destroyed, and it yields no further colour-reactions.

The phenylethyl alcohol which had previously been detected by us as a constituent of champaca oil was also found present in it by Brooks.

Champaca Oil from white flowers (from *Michelia longifolia*, Bl.), In the papers quoted above, Brooks³⁾ also refers to the oil of white champaca flowers. This oil is dark in colour, and has the following constants: $d_{0,897}$, ester v. 180,0, $n_{D_{30}0}$ 1,4470. It contains linalool (identified by its b. p. and by oxidation into citral), methyleugenol (identified by oxidation into veratric

¹⁾ Comp. Knoevenagel, Berl. Berichte **37** (1904), 4041.

²⁾ Journ. Americ. chem. Soc. **33** (1911), 1763.

³⁾ Philippine Journ. of Sc. **6**, A. (1911), 332; Journ. Americ. chem. Soc. **33** (1911), 1463.

acid, m. p. 179 to 180°) methylethyl acetic acid (identified from the silver salt), acetic acid, and traces of a phenol with an odour of thymol.

Chlorocodon root Oil. According to a letter received by us from the Imperial Biological-Agricultural Institute at Amani, *Chlorocodon Whiteii* Hook. occurs in German East Africa in the wild state, and is also cultivated there by the planters for the sake of the hairs which cover the seeds. An experimental steam-distillation of the green root from wild-growing plants had yielded crystals, which were forwarded to us for comparison with those which had been prepared by us (Comp. Report October 1911, 33). They proved, in fact, to be identical with the latter. The pink-coloured crude product melted at about 35°; when recrystallised from water it yielded white crystals which, after being dried *in vacuo* over sulphuric acid, melted between 43 and 45°. The crystals prepared by us at the time, after being again recrystallised and dried over sulphuric acid, gave the same m. p. A mixture of our crystals with those received from Amani showed no depression of melting point.

As mentioned by us in our April Report of 1910, p. 173, P. Friedländer has identified the solid body which has been detected in the root of a *Chlorocodon*-species by E. Goulding and R. G. Pelly¹⁾ as *p*-methoxysalicylic aldehyde. Goulding and Pelly²⁾ have isolated by steam-distillation from root recently received by them from Uganda, about 0,25% of this aldehyde. When condensed with aniline in alcoholic solution the aldehyde yields *p*-methoxysalicylideneaniline, a body which separates in crystals in small yellow plates and has m. p. 67 to 68°.

Oil of Cinnamomum Parthenoxylon. An oil distilled at Buitenzorg³⁾ from the chips of Selasian wood (from *Cinnamomum Parthenoxylon*, Meissn.) gave the following constants: $d_{1,067}$, $\alpha_D + 1^\circ 3'$, sap. v. 8,4, ester v. after acet. 11,8.

Cinnamon Oil, Ceylon (G. Ph. V). The price of this important article, of which the consumption by our customers has enormously increased, has undergone no change during the past winter, in spite of the fact that the tone of the cinnamon market has been quite firm throughout the season, and that on occasion, as for instance at the close of the year, the prices in Ceylon underwent a decided advance. Cinnamon-chips which constitute the principal raw material from which Ceylon cinnamon oil is made, have been wholly unaffected by these fluctuations.

A cinnamon leaf oil prepared at Buitenzorg⁴⁾ contained 74% eugenol sap. v. after acet. 263.

¹⁾ Comp. Report November 1908, 196.

²⁾ Proceed. chem. Soc. 27 (1911), 235.

³⁾ Jaarb. dep. landb. in Ned.-Indië, Batavia 1910, 49. Also comp. Report April 1911, 43.

⁴⁾ Jaarb. dep. landb. in Ned.-Indië, Batavia 1910, 49.

Citronella Oil. With the exception of a few weeks, this article has been able, during the past six months, to maintain the prices at which it stood when our October Report went to press, that is to say from about 1/- to 1/1 cif, with a firm tendency. The reason of this firmness lies probably in part in the decline of the exports as compared with those of the previous year, and in part also in the systematic withholding from the market of the arrivals by the native traders in Matara.

The exports from Ceylon were as follows: —

1 524 275	lbs.	in the year	1911,
1 747 934	"	"	"
1 512 084	"	"	"
1 276 965	"	"	"
			1910,
			1909,
			1908.

The fact that in 1911, as compared with 1910, there was a decline in the shipments of about 13⁰/₁₀ does not necessarily mean that we are faced with a serious falling-off in the supplies or in the output, for, as the figures quoted above show, the shipments in 1911 not only equalled those of 1909, but they even exceeded those of 1908 by about 20⁰/₁₀, in spite of the fact that throughout the year 1911 the cry of short supplies was heard.

It is true, however, that the figures for the present year, so far as they are known, again show a considerable decline, for according to the data at hand the shipments up to 12th February 1912 amounted only to

40 223 lbs. as compared with
173 788 lbs. in the corresponding period of last year.

We are unable to judge in how far this decline is ascribable to the policy of reserve adopted by the native traders, but there are good reasons for assuming that it may be attributed in a large measure to speculation. Whether an upward tendency thus artificially produced can be maintained for any length of time the future must show.

Regular supplies of Java citronella oil have reached us from the producing country and no alterations in price of any kind are to be recorded during the period under review. The sale of this oil to soap-makers has dragged greatly during the last few months; on the other hand, considerable quantities have been consumed by our Department of Artificial Odoriferous Substances, as the oil forms the basis of numerous preparations. There has consequently been no heavy accumulation of stock at our works. We are informed that at a recent fire in Amsterdam 5000 kilos Java citronella oil, which had just been landed, and were stored in a shed, have been burnt.

In addition to the bodies which had long been recognised as constituents of citronella oil, *e. g.* citronellal¹⁾, camphene²⁾, dipentene³⁾, methylheptenone⁴⁾, borneol⁵⁾, geraniol⁶⁾ and methyleugenol⁷⁾, and of valeric acid⁸⁾ (in the ester-form), Schimmel & Co., in the year 1899⁹⁾, detected in the oil the presence of *l*-limonene, linalool (?) and a light and a heavy dextrorotatory sesquiterpene. We are now able to give the results of an examination of an authentic original oil, which examination has yielded many interesting data on the constitution of this important article of commerce.

The material worked up by us consisted of portions of numerous fractions which had been obtained by fractional distillation from a large parcel of oil.

Methylheptenone was found to be present in the first fractions, which boiled over between 120 and 161°. It was separated in the form of the bisulphite compound, and was furthermore identified from the semicarbazone, m. p. 134 to 135°. The surmise that esters might also occur in this fraction, which had been entertained at the outset, proved upon saponification to be unfounded. A fraction with the following constants b. p. 156 to 157,5°, d_{150} 0,8633, α_D — 15°31', was also tested unsuccessfully for α -pinene. A series of reactions, partly intended to detect the presence of other terpenes, again confirmed the occurrence in the oil of *l*-camphene. This examination proved to be particularly interesting because in carrying it out we succeeded for the first time in obtaining from citronella oil camphene in the solid form¹⁰⁾ by fractionation. The portions which boiled over between 160 and 163° consisted almost wholly of camphene. In common with the terpene-fractions boiling between 164 and 168° (d_{150} 0,867 to 0,8635; α_D — 58°13' to — 61°14'), — in which latter we had at first expected to find sabinene or β -pinene, — the fractions in question, when oxidised with permanganate in alkaline solution by Wallach's method yielded camphene camphoric acid, m. p. 142°. The oil which had undergone no change during oxidation turned solid in the cooler during the process of steam-distillation, and after being purified from alcohol exhibited all the characteristics of ordinary camphene. It melted between 49 and 50° [α]_D — 173°22' (in 10,2% solution in chloroform). Fractions which boiled between 160 and 168°, when treated with glacial acetic acid and sulphuric

¹⁾ Berl. Berichte 24 (1891), 210.

²⁾ Journ. f. prakt. Chem. II. 49 (1894), 16.

³⁾ Report October 1893, 15.

⁴⁾ Report April 1895, 26.

⁵⁾ Report April 1894, 17.

⁶⁾ Report October 1893, 18.

⁷⁾ Report October 1898, 18.

⁸⁾ Proceed. Americ. pharm. Ass. 35 (1887), 571.

⁹⁾ Report October 1899, 16.

¹⁰⁾ Report April 1903, 84.

acid, yielded principally *isobornylacetate*, b. p. 70 to 71° (3 to 4 mm.), which upon saponification invariably gave rise to borneol-free *isoborneol*, m. p. 212°. Similarly, when separate fractions were saturated with hydrochloric acid gas, the principal resulting product was invariably the well-known camphene hydrochloride, m. p. about 148°. In spite of these results, however, we must continue to assume that the camphene-yielding fractions of citronella oil also contain considerable proportions of another terpene, perhaps an isomeric camphene, which eventually, in the case of some of the reactions above referred to, is converted into derivatives of ordinary camphene. It should further be stated that when a fraction (d_{150} 0,8636; α_D — 67°46'; n_{D20} 1,47009) was oxidised with alkaline permanganate under ice-cooling, there occurred besides camphene camphoric acid, traces of an acid melting at 180°, which was not identical with succinic acid.

Attempts to establish the presence of phellandrene in a fraction boiling between 170 and 175° (d_{150} 0,8490; α_D — 57°14') and of sylvestrene in fractions boiling between 180 to 182° and 182 to 186° respectively, only yielded negative results. On the other hand, dipentene was found in all the fractions, and one of them also afforded *l*-limonene. The tetrabromides of both terpenes gave the characteristic melting points after fractional crystallisation, and the limonene was furthermore identified from the nitrobenzyl derivative, m. p. 92 to 93°. The above-mentioned fraction boiling between 170 and 175° was also tested for *p*-cymene, and for this purpose was treated with 1% permanganate. The oil which was not attacked, when driven over with steam, had an odour of cymene, but it also possessed a marked optical activity (α_D + 61°10') and when further oxidised under heat it yielded no *p*-hydroxyisopropyl benzoic acid. In order to test for terpinene, the fractions boiling above 175° were saturated in a solution of glacial acetic acid and ether with hydrochloric acid gas and also with permanganate in the presence of alkali, according to Wallach's method. The former reaction gave a hydrochloride, m. p. 49 to 50°, from which after heating with aniline a hydrocarbon was regenerated which, after distillation over sodium, possessed the following constants: b. p. 180 to 182°, d_{150} 0,8544, α_D — 0°3', n_{D20} 1,47821. This hydrocarbon yielded no nitrosite, but when brominated in chloroform solution it afforded a bromide, m. p. about 123°; and is therefore identical with dipentene. The permanganate oxidation-product, a syrup, could not be distilled *in vacuo* without decomposition. The crude product showed no inclination to crystallise. Hence it is probable that citronella oil does not contain terpinene.

The interesting discovery was made that after repeated fractionation it was possible to isolate from the portions containing dipentene terpene-mixtures of a very low sp. gr. These mixtures had a peculiar, estragon-like odour and pointed to the presence of a new terpene. Unfortunately

it was impossible to obtain this body in an approximately pure form, or to identify it from derivatives. Judging from the values disclosed by combustion it appears to be a terpene $C_{10}H_{16}$. In all our experiments we were compelled to work on mixtures which, whether brominated, reduced, or treated with nitrosylchloride, hydrochloric acid gas, or by other methods, yielded derivatives of the dipentene, together with some oily substance. We found, for example, the following constants: b. p. 41° to 41° (4 mm); d_{150} 0,8360, 0,8337, 0,8330, 0,8323; α_D — 32° 41' to 23° 24'; n_{D20} 1,48044. When distilled at atmospheric pressure the body becomes partly resinified. A particularly light fraction (d_{150} 0,8315; α_D — 29° 54'; n_{D150} 1,48287; mol. refr. 46,41, calc. for $C_{10}H_{16}/2$ 45,24) was insoluble in formic acid and when it was attempted to prepare nitrosates and nitrosites did not separate out any solid substances, but only small quantities of dipentene dihydrochloride.

Repeated attempts at reduction with sodium and alcohol, however, yielded hydrated hydrocarbons (d_{150} 0,8115; 0,8182; 0,8077), but the fact that in the course of this reaction comparatively numerous resinous products were formed makes it probable that the latter are reduction-products of dipentene. It was therefore attempted to hydrate the terpene by means of colloidal palladium. The hydrosol-solution was prepared by Paal's method, protalbinat of sodium being used as a protective colloid. The process of reduction was carried out as follows: about 60 g. of the dialysed neutral hydrosol solution (containing about 0,45 g. palladium) was allowed to remain in contact for about 8 hours with 20 g. hydrocarbon (d_{150} 0,8315; α_D — 29° 44') and 120 g. alcohol, during which time hydrogen was passed in and the mixture was strongly turbinated. The liquid very soon turned turbid and palladium was separated off. According to its constants the hydrocarbon had undergone no perceptible change and it was therefore subjected to a fresh reduction under similar conditions, but with a more dilute hydrosol solution, containing a little more protective colloid. The reduction-product was driven off by steam, and distilled as follows: —

	d_{150}	α_D
1. 41° (5 mm.)	0,7989	— 13° 28'
2. 41 to 43° (5 mm.) . . .	0,8084	— 17° 53'

Fr. I had a pronounced odour of lemon. No solid bromide was obtained, either in carbon tetrachloride or in an amyl alcohol-ether mixture. Neither fraction afforded a nitrosochloride. Oxidation with permanganate yielded no products which could readily be identified. The combustion showed that the body was a hydrated terpene: —

0,1534 g. subst.: 0,4874 g. CO_2 , 0,1778 g. H_2O .

Found	Calc. for $C_{10}H_{18}$
C 86,65%	86,96%
H 12,87%	13,04%

Another fraction of the citronella oil with a density of 0,8330 (at 15°) and opt. rot. — 29°59', when hydrated according to Enklaar's method and saponified, yielded considerable first runnings and an alcohol possessing the following characters: b. p. 78 to 80° (5 mm.), d_{15} 0,9180, α_D — 9°44'. Faint terpeneol-like odour. The phenylurethane, at first oily, finally turned solid (m. p. 110 to 111°). Hence the alcohol was impure α -terpineol, owing its generation probably to the dipentene or limonene which was admixed to the fraction. Further particulars concerning the new terpene must be reserved until after subsequent examination.

The fractions with higher boiling points than the terpene fraction consisted chiefly of citronellal, but they contained, besides considerable proportions of borneol, certain other compounds with somewhat characteristic odours, including a body with a peculiar linalool-like aroma, but which was not identical with linalool. We have not yet succeeded in identifying this body from its derivatives. It was discovered in the portions boiling between 81 and 85°, sp. gr. 0,9122, after they had been freed from citronellal with bisulphite, and from borneol by freezing. No phenylurethane was formed, but oxidation with bichromate and sulphuric acid gave rise to citral, b. p. 89 to 91° (3 to 4 mm.). The characteristic citralidene cyanoacetate had m. p. 120 to 121°. Another fraction, b. p. 71 to 75° (d_{150} 0,8982) when acetylated, afforded an oil, b. p. 72 to 74° (4 mm.), with an odour of linalyl acetate, but, again, the saponified product yielded no phenylurethane, although it was oxidisable into citral. From the above it may however be concluded (contrary to our previous experience)¹⁾ that linalool is not a constituent of citronella oil. We hope to be in a position, later on, to make further communications on this subject. The chromic acid oxidation-product mentioned above, which did not react with bisulphite, was found to contain an oil with a thujone-like odour, which reacted in part with semicarbazide. Possibly the semicarbazone recrystallised from methyl alcohol, m. p. 179 to 182°, was a derivative of thujone. We also attempted, by oxidising with permanganate, to prepare from a fraction boiling between 202 and 210° (d_{150} 0,9121), with a faint odour of thujyl alcohol, the thuja keto acid, m. p. 76°, but were unsuccessful.

The high *l*-borneol content of the succeeding fractions greatly militated against their being tested for other alcohols. Unfortunately our endeavours to eliminate this troublesome product by chemical means, *e. g.* chloral remained without the desired result. The *l*-borneol, m. p. 200 to 203°, which was obtained by freezing-out was found, when oximated, to be free from camphor.

In a fraction boiling between 218 and 230°, which had been freed from borneol as far as possible, we ascertained the presence of nerol, albeit in inconsiderable proportions. This body was accumulated in an

¹⁾ Report October 1899, 16.

alcohol mixture which had been separated from the solution of the phthalic ester salt by repeated treatment with calcium chloride, and after being again purified by means of phthalic anhydride it was obtained after saponification in the form of an oil, b. p. 98 to 101° (6 to 7 mm.) to which faint borneol odour still adhered. It was positively identified as nerol from the tetrabromide, m. p. 116 to 118°. The neryldiphenylurethane was not obtained in an entirely pure form; it only melted between 55 and 57°. The oil which contained nerol also contained a compound from which water was given off when distilled under atmospheric pressure. It would seem, however, that citronellol, which should have been present in these fractions, did in fact not occur therein. In lieu of the silver salt of the acid phthalate (m. p. about 126°) which is characteristic of citronellol, repeated examination only afforded in every case the geraniol derivative melting at 133°. Hence, in corroboration of the results previously obtained by us¹⁾, it may now be held to be tolerably certain that Ceylon citronella oil contains no *free* citronellol. But on the other hand we ascertained that citronellol is actually present in the oil in the form of *d*-citronellol, as esters (for instance, acetic ester), and certainly also a butyric ester, in such proportions, indeed, that it can scarcely be overlooked if the oil is carefully tested. The alcohol was isolated by treating the saponified oil-portions boiling between 86 and 88° and between 88 and 94° (3 to 4 mm.) and sp. gr. 0,8805 to 0,8884 with phthalic anhydride in benzene solution after previous elimination of the geraniol by calcium chloride. The alcohol, which contained small proportions of borneol, showed the following constants: b. p. 84° (3 mm.), d_{150} 0,8725, $\alpha_D + 0^\circ 13'$, b. p. 84 to 85° (3 mm.), d_{150} 0,8696, $\alpha_D + 1^\circ 17'$. Another sample, which had been further purified from primarily produced formate possessed the following properties: d_{150} 0,8661, $\alpha_D + 1^\circ 52'$, n_{D20} 1,45891, b. p. 92 to 93° (5 mm.). The silver salt of the phthalate possessed the required m. p. 125 to 126°.

The present examination has also failed to supply any indication of the presence of terpineol in citronella oil. When tested for geranyl acetate it was found that it was possible to accumulate the oil only to a very slight extent by fractionation *in vacuo* into those portions of which the b. p. would indicate the presence of geranyl acetate (sap. v. 64 to 76°) because mixtures of borneol, nerol, geraniol, esters, a hydrocarbon, and others, were present. But in any case, the odour of an acetic ester fraction b. p. 96 to 98° (4 to 5 mm.), sap. v. 85, together with the fact that the geraniol content was undoubtedly increased after saponification, warranted the conclusion that geranyl acetate was also present in the fraction under examination.

¹⁾ Report October 1899, 20.

Analysis of the silver salt of the acetic acid boiling at about 120° :

0,2729 g. subst.: 0,1758 g. Ag.

Found
Ag 64,42%

Calc. for $C_2H_3AgO_2$.
64,67%

The acid mixture which was isolated from the saponification liquors of the ester fractions which had served to afford the test for the presence of citronellol, as well as from the higher boiling oil fractions, contained in those of its portions which boiled above 130° an acid of which the b. p. was about 65° (7 mm.). At ordinary pressure this acid passed over constant at 163° ; and by its odour likewise it was recognised as *n*-butyric acid. It solidified into crystals when placed in a freezing mixture. Its chloride boiled between 35 and 36° (7 mm.) and, with ammonia, was converted into *n*-butyric amide, m. p. 114 to 115° . Valeric acid, which is said to occur in citronella oil, could not be isolated up to the present. The distillation-residue of the acid mixture which remained behind was a solid yellowish acid, crystallising from water in the form of needles, m. p. about 180° ; this acid was not identical with veratric acid.

Those portions from the preparation of citronellol which gave no reaction with phthalic anhydride, and of which the b. p. lay between 85 and 90° (4 mm.), contained a hydrocarbon with an odour resembling that of petroleum. By treating this substance with benzoyl chloride and pyridin its alcoholic constituents were eliminated. The body, when heated *in vacuo* with sodium, possessed the following properties: b. p. 95 to 96° (5 mm.), b. p. 249 to 252° , d_{150} 0,8924, $\alpha_D - 13^{\circ} 2'$, n_D 1,49281. Combustion showed it to consist of a sesquiterpene $C_{15}H_{24}$, probably contaminated with a slight proportion of methyleugenol, which is well-known to be the principal constituent of the high-boiling fractions of citronella oil. No derivatives such as a nitroso chloride, nitrite, nitrosate or hydrochloride were obtainable. When the body was brominated in chloroform solution there was a strong evolution of hydrobromic acid. In view of the difference in the constants it is questionable whether this body is identical with the light sesquiterpene of citronella oil of which the presence was detected by us several years ago¹⁾. We have not gone into a further examination of the fractions, which consist principally of methyleugenol and of the dextrorotatory sesquiterpene of which the presence has also already been established on a previous occasion.

The examination detailed above has therefore shown that Ceylon citronella oil contains the following bodies in addition to those previously known: a hydrocarbon of low specific gravity (terpene?), a body related to linalool, an alcohol which may be found to be identical with thujyl

¹⁾ Report October 1899, 23.

alcohol, nerol, *d*-citronellol (but only in the form of acetic and of *n*-butyric ester), geranyl acetate and a high-boiling lævorotatory hydrocarbon $C_{15}H_{24}$.

It is certain that neither linalool nor valeric acid can be counted among the constituents of the oil.

On p. 35 of our last Report we commented upon certain criticisms to which an acetylation-method for citronella oil, published in *The Chemist and Druggist*, had been subjected by C. Kleber. It would appear that the English chemists concerned in the matter have been far from edified by Kleber's criticism, and still less by the fact that we had been so bold as to reproduce its essential features in our Reports, for soon after the publication of our last Report, articles appeared in two English journals¹⁾, and subsequently in an American publication²⁾, in which our arguments were contradicted in a more or less aggressive manner. Before dealing further with the contents of these articles, we desire to place on record that it is our practice to refer to the published work of other authors purely from an impartial standpoint, taking as our sole guide the importance of the publication, and disregarding altogether whether our references are or are not palatable to third parties. This principle will also continue to guide us in the future.

Our rejoinder to the comments of the English chemists may be compressed within a fairly brief compass, since all these comments are written from the same point of view, and differ from each other only in the tone in which they are couched. With regard to the latter, Mr. Umney, the author of the article in *The Perfum. and Essent. Oil Record*, undoubtedly carries off the palm, for the spiteful manner in which he treats not only the subject under discussion, but also other parts of our Report, is surely without parallel. In fact, we should have altogether abstained from replying to him, were it not that this might be construed as an admission on our part that Mr. Umney's criticisms were justified, and *that* we do not admit by any means.

Both Umney and Parry continue to defend the standpoint that in the course of the process of acetylation, water is formed, and in proof of this, Umney even sets up a chemical equation which as Kleber³⁾ observes very pertinently in a rejoinder dealing with the same subject, looks very fine on paper, but unfortunately does not correspond with the facts. For in reality it is not two molecules of alcohol, as Umney and Parry believe to be the case, but one molecule which reacts with 1 molecule acetic anhydride, giving rise to the corresponding ester and acetic acid. In this process, therefore, no water is formed at all, hence the added

¹⁾ Chemist and Druggist 79 (1911), 749; Perfum. and Essent. Oil Record 2 (1911), 259.

²⁾ Parry, Americ. Perfumer 6 (1911), 227.

³⁾ Americ. Perfumer 6 (1911), 228.

sodium acetate does not play the part of a dehydrating agent, which Umney and Parry would fain assign to it.

The authors in question also take umbrage at our entire agreement with Kleber's suggestion that for the sake of clearness fused sodium acetate should be prescribed for the acetylation, and they attempt to fight us with our own weapons by pointing out that we ourselves have always recommended dry sodium acetate for this purpose, and that this same substance is mentioned both in the first and in the second edition of our book *The Volatile Oils*. We admit this at once, but with the best will in the world we cannot see that this is inconsistent with our regarding Kleber's recommendation as fully justified, for although to the chemist "dry sodium acetate" may mean the anhydrous salt, we are of opinion that there is no harm whatever in expressing oneself somewhat more clearly and using the term "fused sodium acetate", particularly so since it has been shown that the term "dry" sodium acetate has been misunderstood by American chemists¹).

We simply do not understand why Messrs. Parry and Umney should look upon Kleber's proposal as if it were so to say a personal insult. In any case we trust they will conclude from our admission that we are always very ready to make concessions when they appear to us to be to the purpose. It was obedience to this principle which caused us at the time (Report April 1910, 154) to advocate the two hours' acetylation of citronella oils after de Jong had drawn attention to the fact that an acetylation of one hour gave too low values.

Fault has also been found with us because we have not adversely criticised Kleber's suggestions relating to the washing-out of the acetylation-mixture, and in this connection also Parry endeavours to convict us of contradictory views by quoting passages from our above-mentioned book. Parry, however, has altogether overlooked the fact that when reproducing Kleber's recommendation in our last Report (p. 36), we referred in a footnote to our book, with the intention — needless to say — of showing that we ourselves do wash out the acetylation-mixture. As it is possible to do this by different methods without thereby altering the acetylation-prescription itself in any way, and without giving rise to errors, there was no reason whatsoever why we should disparage Kleber's method.

But the suggestion made by the English chemists that the acetylated oil should only be saponified for the space of half an hour is a very different matter. We certainly do protest against such a modification, and that on the ground of experiments carried out by us with mixtures of known geraniol- and citronellal-content, which showed that half an hour's heating with semi-normal-potash liquor is not sufficient for purposes of quantitative saponification. We did not specially mention this

¹) Kleber, *ibidem* 229.

at the time of our experiments (Report April 1910, 154) because we regard it as a matter of course that the oil should be saponified for at least one hour. But as Parry lays stress upon the fact that according to his experience geranyl acetate is completely saponified after half an hour we may further add that this does not apply to *isopulegyl* acetate, into which citronellal is converted by acetylation. This we have also ascertained in experiment. With a freshly-prepared and carefully purified *isopulegyl* acetate a constant ester value of $281,9 = 98,7\%$ ester was only obtained after one hour's saponification. When heated for a longer period the ester value was not increased, whereas after half an hour's saponification the ester value was only $276,3 = 96,7\%$ ester.

We certainly cannot acquit the English chemists of the charge of not having paid sufficient attention to our recent publications, especially to those relating to the acetylation of citronella oil, and when the Editor of *The Chemist and Druggist* asserts that the acetylation-method of the English chemists is also based upon experiment, we ask where the experiments with mixtures of known geraniol- and citronellal-content which are said to have been made by *English* chemists are published? For only by such experiments is it possible to solve the question: not by acetylation tests with citronella oils. In the interests of the subject itself, and in spite of Mr. Umney's indignation, we shall continue deeply to regret that in our view arbitrary deviations on the part of the English chemists from our acetylation-method. It is to be hoped that in further discussions on the subject Mr. Umney will adopt a controversial style which is more becoming and to the point, as we should otherwise feel compelled to refrain from replying to his publications. In order to set his mind at ease we declare once more that we are, and always have been, very sympathetic indeed towards the geraniol-test as such, and that our sole reason for advocating Schimmel's simple and stricter test is because we doubt the possibility of a general commercial application of the geraniol-test for the present (comp. Report April 1911, 45). If, however, Messrs. Umney and Parry should refuse to understand us, and should persist in distorting our statements, we can only admit that we are powerless to prevent it.

Two slight misunderstandings should not be passed unnoticed. The Editor of *The Chemist and Druggist* appears to believe that in the acetylation of citronella oil the objective is the evaluation of the esters in the oil, whereas in point of fact the purpose of the acetylation is to determine the geraniol- and citronellal-content. And against Kleber's view that warming of the ready washed-out, acetylated oil on the water-bath with sodium bisulphate is superfluous, to say the least, Parry quotes the acetylation-method described in the new edition of our book *The Volatile Oils* (p. 594), in which it is stated, *inter alia*, that for the purpose of decomposing the excess of acetic anhydride the acetylation-mixture should

diluted with a little water and warmed for 15 minutes on the water-bath with frequent shaking. We do not quite follow this argumentation.

As already stated above, Kleber has also published a reply to the articles of Parry and Umney, but a bare mention of this fact will suffice here, as quotation would only involve repetition.

In connection with the above we may briefly refer to a paper by Th. H. Durrans¹⁾ in which a special acetylation-method for Java citronella oil is given, as in Durrans' opinion the method of Umney and Parry is only applicable to Ceylon citronella oil. With regard to this we may point out that the method described in our April-Report of last year (p. 46) yields accurate results both with Ceylon and with Java oil.

In the April number of *The Tropical Agriculturist* there appeared an article by N. Wickremaratne on the citronella oil industry in Ceylon, of which abstracts are given in *The Chemist and Druggist* [79 (1911), 443]. From the last-named journal we quote the following details, in which unavoidably a good deal of familiar ground is included. It is estimated that there are at present in Ceylon 40 000 acres under citronella grass, the total number of stills in operation being about 500. Formerly the principal centre of the industry was in the district of Galle, but at present the cultivation of the grass is restricted to the district of Matara and part of the district of Hambantota. Lena-batu grass is chiefly grown. It is very hardy and yields the variety of citronella oil which is characteristic of Ceylon. The seedlings are planted out at distances of from 1 to 2 feet and after 8 months the grass is ripe for cutting, after which cutting can be repeated every third month. It is done by women with an ordinary sickle. The cut grass, after lying in the sun for a day to dry, is taken to the distilleries. If it should be necessary to keep it there for some time before it is distilled care must be taken not to stack it in high heaps, as otherwise fermentation sets in, resulting in a loss of oil. The distillation is carried out on modern principles; earthenware stills, such as were employed many years ago, are now scarcely seen. The size of the stills varies greatly, their capacity ranging from 700 to 2000 lbs. of grass. Ordinarily each plant has two stills, which are worked alternately so that the distilling itself is not interrupted by the emptying and filling of each still. Two charges are worked up daily, each distillation requiring about six hours. The exhausted grass is used as fuel for the boiler.

Cooling is done in the usual way, the length of the condensing-worm varying from 30 to 60 feet. The oil separates from the water in the receiver and is skimmed off with a cup, while the water, as in a Florentine flask, runs off below. Before the oil is placed in tins for shipment it is filtered several times.

¹⁾ *Perfum. and Essent. Oil Record* 2 (1911), 201.

Wickremaratne estimates the total yield per acre and year (four cut at 18000 lbs. grass and, when the grass is in good condition, at 68 lbs. of oil).

In our April Report of last year (p. 48) we referred to an article on *Andropogon-* (*Cymbopogon-*) oils which had appeared in the *Circulars and Agricultural Journal of the Royal Botanic Gardens, Ceylon* (Vol. V, No. 1, November 1910, 115). The results of the investigations there recorded have since been published also in the *Bulletin of the Imperial Institute* [9 (1911), 240, 333.]

According to a communication by the Imperial Institute¹⁾ in London a sample of citronella oil received from the Gold Coast possessed the following characters: d_{15}^{20} 0,903, $\alpha_D + 2^\circ 56'$, total geraniol 76% (geraniol 33,9%, citronellal 42,1%), sol. in 2,8 vols 70% alcohol and in 1,4 vol 80% alcohol. The oil was of a pale yellow colour. The parent-plant is thought to be *Cymbopogon Winterianus*.

Oil from the leaves of *Citrus Hystrix*. According to Brooks²⁾ the leaves of *Citrus Hystrix*, D. C. yield a maximum of 0,08% of an essential oil possessing the following constants: d_{30}^{30} 0,9150, $\alpha_D - 10,50^\circ$, n_{D30}^{30} 1,4650, sap. v. 50,2. Its odour resembles that of shaddock-leaf oil (vide p. 116).

Oil of *Clausena Anisum-olens*. As stated in our Report of October 1909 (p. 145), the leaves of *Clausena Anisum-olens* (Blanco), Merrill possess, according to Bacon, a strong odour of Russian anise, for which reason they as well as their alcoholic extract, are employed on the Philippines in the preparation of liqueurs. Brooks³⁾ obtained from the leaves of this Rutaceae a yield of 1,16% of a colourless oil possessing the following constants: d_{30}^{30} 0,963, $\alpha + 0$, n_{D30}^{30} 1,5235, sap. v. 3,6. It consisted to the extent of from 90 to 95% of methylchavicol, which was identified by oxidation into homoanisic acid (m. p. 84 to 86°).

According to Brooks, certain kinds of cigarettes made in the Philippines are scented with the leaves of *Clausena Anisum-olens*.

Clove Oil. The result of the winter-crop 1911/1912, which even at the time of our last Report promised to be favourable, is probably not over-estimated at 200000 bales, which is equal to an excess of about 70000 bales over that of the previous crop. Yet, in spite of these figures, the prices have not receded to the extent expected, which is no doubt to be ascribed to the fact that within the past few weeks somewhat important sales have been effected both in London and in Hamburg. These sales

¹⁾ Bull. Imp. Inst. 9 (1911), 253.

²⁾ Philippine Journ. of Sc. 6, A. (1911), 349.

³⁾ Philippine Journ. of Sc. 6, A. (1911), 344.

are probably connected with the circumstance that in view of the result of the crop buyers at first manifested great reluctance in placing orders, but were finally compelled to come into the market in order not to remain bare of supplies. If no unforeseen incidents occur it is likely that the prices will further recede, especially because recent advices depict the present prospects for this year's summer-crop as very favourable. The prices of clove oil were regulated in the course of the winter by the position of cloves, but they were in part maintained owing to the development of a fairly brisk business for delivery. Extremely low and purely speculative offers proceeding from a certain quarter finally caused a feeling of some uncertainty, but it remains to be seen whether these apparently favourable offers will prove in the end to have been of advantage to the consumers. We have our doubts on this point.

The trade in clove-stems has also been fairly brisk. The bulk of this article continues to be used in the manufacture of vanillin, but it appears to us that just at present the price of clove-stems is too high in proportion to that of cloves.

In completion of the already available statistical material we here reproduce the Report on cloves supplied by the German Consulate at Zanzibar. The report, which covers the year 1910, has made its appearance with the customary delay¹⁾.

The exports of cloves from Zanzibar have been as follows: —

	Quantity (lbs.)	Value (Rupees)
1906	15 105 760	5 349 545
1907	18 214 668	5 941 817
1908	14 974 872	3 974 398
1909	20 285 001	4 956 142
1910	12 783 149	3 802 048

The exports of cloves in 1910 amounted to 25,6% of the total exports. The clove shipments were distributed as follows: —

	1906	1907	1908	1909	1910
	Quantity (lbs.)				
Europe	8 939 789	10 457 830	7 197 375	10 638 889	4 800 676
U. S. A.	717 909	1 102 420	651 780	2 364 940	1 096 215
Asia	5 355 875	6 553 453	7 051 342	7 193 252	6 758 231
Africa	92 192	100 965	74 375	97 920	128 019
	Value (Rupees)				
Europe	3 176 924	3 387 448	1 894 363	2 596 630	1 323 287
U. S. A.	238 975	306 061	184 578	589 911	303 592
Asia	1 901 368	2 215 262	1 876 332	1 746 728	2 138 243
Africa	32 278	33 046	18 725	22 843	36 926

¹⁾ Deutsches Handelsarchiv, February 1912.

The shipments to European markets were distributed as follows: —

	1906	1907	1908	1909	1910
	Quantity (lbs.)				
Rotterdam	1 543 310	952 006	560 351	3 007 720	1 685 900
London	2 650 919	3 298 930	2 283 330	1 592 492	565 829
Hamburg	3 841 300	5 529 050	3 296 968	4 498 151	2 177 370
Marseilles	585 760	418 850	894 986	1 041 827	188 467
	Value (Rupees)				
Rotterdam	557 320	295 300	141 704	712 148	432 425
London	915 629	1 112 693	600 075	405 447	215 019
Hamburg	1 387 202	1 770 961	886 785	1 111 183	560 317
Marseilles	207 338	125 867	225 757	250 876	59 251

The percentage-proportion of the principal countries was as follows: —

	1906	1907	1908	1909	1910
	%	%	%	%	%
India	33,3	36,3	46,0	32,32	55,5
Germany	25,9	29,8	22,3	25,9	14,75
Netherlands	10,9	4,9	3,6	13,7	11,4
U. S. A.	5,4	5,1	4,6	11,4	8,0
United Kingdom	17,0	18,7	15,1	7,9	5,6
France	3,8	2,1	5,7	4,7	1,5

As on previous occasions, it is pointed out that the Customs Statistics declare Germany to be the country of destination of all cloves shipped in German bottoms, whereas the B/L is usually made out with option Rotterdam/London. London being the world's market for cloves, the greater part of the cloves shipped to Germany actually goes to London and not to Hamburg.

The following table gives a review of the clove-crops of the last 10 years (the crop season in each case being August—July).

	Island of Zanzibar Frasilah	Island of Pemba Frasilah	Total Frasilah	Average yearly price Pemba		
				Rupees	Annas	Pies
1901/02	43 626	321 599	365 225	6	6	6
1902/03	175 420	251 780	427 200	6	8	6
1903/04	28 369	96 792	125 161	13	4	—
1904/05	79 860	675 683	755 543	9	5	6
1905/06	181 536	109 931	291 467	11	14	3
1906/07	56 833	202 633	259 466	13	—	—
1907/08	141 850	299 952	441 802	9	9	—
1908/09	165 733	449 685	615 418	8	5	—
1909/10	160 000	320 000	480 000	9	12	—
1910/11	52 002	139 301	191 303	10	5	—

The above prices refer to Pemba-cloves only; the price of Zanzibar-

cloves rules a little higher. The exports of clove-stems in 1910 amounted to 2 304 958 lbs., of the value of 185 723 Rupees. They were distributed as follows: —

	1906	1907	1908	1909	1910
	Quantity (lbs.)				
Europe	2 317 305	2 055 415	2 361 964	4 318 057	2 262 293
U. S. A.	—	179 900	552 160	186 620	—
Asia	63 056	48 125	34 787	42 035	42 665
Africa	2 065	—	—	—	—
	Value (Rupees)				
Europe	222 608	190 197	172 398	278 905	182 356
U. S. A.	—	15 060	39 972	12 669	—
Asia	6 831	4 708	2 418	3 024	3 367
Africa	285	—	—	—	—

The greater part of the exports in the year under review, as in previous seasons, went to Hamburg.

We have also recently received a sample of the first clove crop from Amani (German East Africa) which yielded 16,6% of an oil possessing the normal properties set forth below: d_{15}° 1,0558, $\alpha_D - 1^{\circ} 4'$, n_{D20}° 1,53204, phenol-content: 92%, soluble in 1,2 vols a. m. 70% alcohol.

A sample consignment of clove-stems from the same place yielded only 5,3% oil, which, however, was equal in quality to the other commercial varieties: d_{15}° 1,0515, $\alpha_D - 0^{\circ} 58'$, n_{D20}° 1,53461, sol. in 1,1 vol. a. m. 70% alcohol. Unfortunately the quantity of oil distilled from the sample was too small to admit of an estimation of its eugenol content.

A few years ago we repeatedly had occasion to describe in our Reports clove-leaf oils from the Seychelles¹⁾, and we are now also in a position to report on clove oil proper from the same islands, as we have recently received several samples of Seychelles cloves, which we have worked up for oil. Two of these distillates gave the following constants: d_{15}° 1,0470, 1,0485, $\alpha_D - 1^{\circ} 30'$, $-1^{\circ} 6'$, phenol content 85 and 86% respectively. Both oils were soluble in 1,5 vols. 70% alcohol, but upon the addition of 4 vols. of the solvent the mixture turned cloudy. In respect of imperfect solubility, therefore, the oils behaved similar to an oil distilled by us from Amboina cloves²⁾. This oil, it will be remembered, while behaving normally in other respects, also gave a clear solution at first in 70% alcohol, but solutions of somewhat pronounced turbidity with 2 to 4 vols.

¹⁾ Report October 1907, 37; November 1908, 48.

²⁾ Report October 1904, 22.

Copaiva Balsam Oil. The balsams which are used in the preparation of Pará copaiva balsam oil were occasionally very scarce, and the oil content of the imports in particular very often left much to be desired. The price has undergone a corresponding increase and appears likely for the present, to be maintained at the advanced figure. Pará copaiva balsam oil has lately found a regular outlet as an artists' material for painters' use, and appears to be found serviceable for that purpose.

In our Report of October 1910, p. 40, we mentioned a method of testing copaiba balsam recommended by Cocking, which is based, *inter alia*, upon the feature that the optical rotation of the essential oil separated from genuine balsam is invariably somewhat higher than that of the first 10% distilled from the oil *in vacuo*. Cocking's method is intended to serve as a means of detecting an addition of African copaiba balsam as well as of Gurjun balsam, and has been recommended for adoption in the British Pharmacopœia.

Parry¹⁾, while examining several samples of Maracaibo balsam from an undeniably reliable source has found that they did not correspond with Cocking's requirements; on the contrary, in two samples the first 10% of the oil, obtained by steam-distillation, showed a higher optical rotation than that of the bulk of the sample, while in a third sample the two rotations were exactly equal. The optical rotations of the separate fractions of the oils compared with each other also deviated somewhat from the values recorded by Cocking. Parry regards adulteration of the samples examined by him as out of the question, the more so because the deviations were so slight that, if any adulteration were present, it could only have been so small as not to be worth the trouble.

Parry is of opinion that, in order to discover whether Cocking's method is really valuable, it would be necessary to examine a larger number of samples of different origin. If this were done it would of course be necessary also to lay down the conditions of distillation with great precision, and in all cases to carry out the separation of the oil from the resin by steam-distillation, as any other distilling-method would give rise to decomposition-products which would affect the rotation. Parry found that the optical rotation of an oil distilled from the balsam *in vacuo* was 3.5° lower than that of an oil prepared from the same balsam by steam distillation.

Cocking²⁾, in a rejoinder, denies the last-named assertion of Parry's. Cocking has ascertained by experiment that it makes no difference whether the oil is separated from the resin by distillation in steam or *in vacuo*, and in proof of this contention he quotes the results of comparative ex-

¹⁾ Chemist and Druggist 80 (1912), 19.

²⁾ *Ibidem* 128, 204.

periments. The optical rotations, both of the volatile oils and of the corresponding fractions, showed but slight differences, the values, taken in their entirety, being practically the same in each case. For distillation *in vacuo* Cocking uses a large splash-head of special design, of which a sketch is given in his article, and by which any bumping-over of the contents of the flask is obviated. Distillation is continued until the manometer commences to fall, the fall indicating the commencement of the decomposition of the distillation-residue.

Cocking again asserts that in his experience the volatile oils from all genuine copaibas have a higher rotation than the first 10% distilled *in vacuo* from them. With several samples which gave the reactions for Gurjun balsam, and in which the proportion of the adulterant was estimated to be from 5 to 6%, the distillation-test yielded results similar to those obtained by Parry with Maracaibo balsams.

Coriander Oil. Contrary to all expectations, and in spite of the fact that the failure of the crop might have been held to warrant a serious advance, the prices of coriander oil have continued to move within moderate limits. The reason of this is no doubt that the demand for the oil has fallen off considerably. We have already on a previous occasion drawn attention to this fact, and recent experience has confirmed our observation. As a result of this reduced consumption the prices have remained on the same level as last autumn, and our fear of a further increase has fortunately not been realized.

Costus Root Oil. We again draw attention to the exquisite oil distilled by ourselves and we invite our friends to ask us for special quotations when important quantities are required. We are in a position to supply costus root oil very cheaply indeed.

In the *Seifensieder Zeitung und Revue über die Harz-, Fett- und Öl-industrie* [39 (1912), 160] there is an article by H. Mann on the use of costus root oil in perfumery from which we take the following: Although costus root oil imparts a touch of distinction to articles prepared with it, it is but little used, probably, in part, because it cannot always be procured. The odour of the freshly-distilled oil is at first not exactly pleasant, but gradually it develops a most agreeable violet-like aroma, which also helps to fix other odours. The employment of old oil is not to be recommended, as it possesses an unpleasant accessory odour, which easily penetrates other odours, and thus has a predominant effect. It is advisable to stock the oil in the form of a 10% alcoholic solution. Used in conjunction with vanillin and Portugal oil in particular it produces excellent scents. Many French powders owe their popularity to the odour of costus root oil.

Cubeb Oil. The high prices have remained unchanged, for there has been no alteration whatever in the position of the cubeb market. The

arrivals are quite insufficient for the requirements, and it is said that numerous former producers have abandoned the cultivation of cubebs because it has not paid them in past years when the prices were low. It might be thought that in the meantime they would have learnt to know better, for the values which have now ruled for cubebs for many years should surely, we think, induce planters to take up the cultivation with renewed energy.

Cypress Oil. Since we have taken up in our factory at Barrême the preparation of cypress oil by the method in vogue at our Miltitz works, we have always at our disposal freshly-distilled oil such as we consider necessary for the successful treatment of whooping-cough. Within the past ten years cypress oil has become an indispensable article in the therapy of this disease, its application being as simple as its effect is rapid and completely effective. It is to be hoped that many specialists in this branch of medicine will convince themselves by practical experience of the virtues of this remedy, and we shall always be pleased to supply literature on the subject.

Dutch Myrtle Oil. This oil, from *Myrica Gale*, L. (N. O. Myricaceæ) of the constituents of which practically nothing has been known so far has been subjected to closer investigation by S. S. Pickles¹). A pale yellow oil distilled from a mixture of green leaves and branches (yield 0,076%), gave the following constants: d_{150} 0,915, α_D — 5° 17', acid v. 7,0 sap. v. 31,7, ester v. 24,7. A distillate obtained from half-dried material almost entirely consisting of leaves (yield 0,203%) possessed the following properties: d_{150} 0,912, α_D — 11° 26', acid v. 4,0, sap. v. 23,2, ester v. 19,2 ester v. after acet. 56,4.

The leaf-oil contained about 0,75% of a paraffin $C_{29}H_{60}$, m. p. 63 to 64° which separated out in the cold when methyl alcohol was added. By treating the oil with soda solution, Pickles isolated from it about 2,5% fatty acids, principally palmitic acid (m. p. 62°). Further constituents are cineole (m. p. of the iodol-compound 112 to 114°) and dipentene (m. p. of the tetrabromide 124 to 125°). The oil contains about 50% cineole and terpenes. In addition to the esters of high-molecular fatty acids the oil probably contains a mixture of high-boiling alcohols and sesquiterpenes which, however, has not been more closely examined by Pickles for lack of sufficient material.

Some time ago Laloue²) published detailed particulars concerning the properties of Dutch myrtle (Dog myrtle) oil. Chevalier²) has tested the pharmacological action of the oil.

Elecampane Oil. So far but little is known of the properties of oil of elecampane, and it may therefore be of interest here to record the

¹) Journ. chem. Soc. 99 (1911), 1764.

²) Comp. Report October 1910, 42.

constants of a distillate recently prepared by us from the root of the plant. The product appeared in the form of a mass of colourless needles, saturated with a small proportion of a brown oil, and deliquescent into a brown liquid at from 40 to 45°. Its odour is peculiar, perhaps somewhat like that of ladanum. The high sp. gr. of 1,0374 at 30° and the pronounced optical activity ($\alpha_D + 123^\circ 45'$) are worthy of note. The other constants determined by us are: acid v. 6,4, ester v. 180,0, ester v. after acet. 199,0.

Essential Oils, Sicilian and Calabrian.

Our esteemed friend, Mr. Eduardo Jacob of Messina, reports in his customary obliging manner as follows:—

The exports in the year 1911 have exceeded those of the previous year by 137 476 kilos, value 3 709 065 Lire. The shipments have not only absorbed the entire production of the year 1911, but have also reduced from over 100 000 kilos to about 30 000 kilos the stock of old lemon oil which was carried over from the year 1910 into the year 1911. These circumstances gave rise to a general advance in prices in Sicily, until the quotations far exceeded the average of last year. It is not surprising that the first outcome of this advance in prices was that the stocks in foreign countries were used up to the last drop, and the next that during the closing months of the year consumers abroad made their purchases in the producing country with the utmost circumspection and so to speak from hand to mouth only. The fact that in spite of these precautions the stocks in Sicily have likewise been cleared, except for the small balance mentioned above, shows that the world's consumption is steadily expanding. In these circumstances the closing months of 1911 have witnessed an animated business for delivery abroad in 1912, as everywhere there has been a perceptible lack of available oil. The essence trade of Calabria and Sicily has therefore entered upon the year 1912 under exceptionally favourable auspices.

Bergamot Oil. In September of last year this article was quoted at from 42 *M* to 43 *M*, and throughout the months of September and October it remained approximately at that level, while the available oil, almost to the last drop, passed into the hands of the consumers.

During the four or six weeks preceding the arrival of the new oil the old stocks had been cleared to such an extent that a few stubborn holders, who up to that time had refused to sell, were able to realize as much as from 50 *M* to 52 *M* for their wares.

It is true that on the whole the new crop was not expected to yield a favourable result, but the manufacturers nevertheless believed that by selling at from 40 *M* to 41 *M* they were reasonably sure of a decent

Exports of Essential Oils in the year 1911.

Country of Destination	1910		1911	
	Kilos	Lire	Kilos	Lire
a) Messina:				
North German Ports	6 854	137 080	5 238	104 760
Austria-Hungary	18 313	366 260	46 004	920 080
Belgium	2 510	50 200	1 980	39 600
Denmark	1 130	22 600	1 280	25 600
France	12 576	251 520	39 901	798 020
Greece	—	—	—	—
United Kingdom	60 104	1 202 080	92 677	1 853 540
Netherlands	600	12 000	2 875	57 500
Russia	4 648	92 960	6 363	127 260
Sweden	1 290	25 800	1 120	22 400
Norway	200	4 000	180	3 600
Spain and Portugal	—	—	—	—
Turkey	670	13 400	298	5 960
U. S. of America	55 644	1 112 880	236 021	4 720 420
South America	1 540	30 800	1 868	37 360
Australia	6 068	121 360	13 201	264 020
Egypt	483	9 660	425	8 500
India	916	18 320	510	10 200
Italy	1 630	32 600	7 435	148 700
Other countries	640	12 800	336	6 720
Total	175 816	3 516 320	457 714	9 154 280

b) Catania:				
North German Ports	9 580	191 600	3 057	61 140
Austria-Hungary	20 865	417 300	13 152	263 040
Belgium	1 960	39 200	1 880	37 600
Denmark	233	4 660	1 840	36 800
France	15 749	314 980	10 835	216 700
Greece	—	—	—	—
United Kingdom	19 038	380 760	15 117	302 340
Netherlands	3 739	74 780	2 245	44 900
Russia	1 813	36 260	1 268	25 360
Sweden	—	—	720	14 400
Norway	—	—	295	5 900
Spain and Portugal	130	2 600	460	9 200
Turkey	—	—	595	11 900
U. S. of America	168 282	3 365 640	74 874	1 497 480
South America	250	5 000	390	7 800
Australia	3 280	65 600	2 142	42 840
Egypt	—	—	—	—
India	—	—	—	—
Italy	—	—	—	—
Other countries	6 857	137 140	271	5 420
Total	251 776	5 035 520	129 141	2 582 820

Country of Destination	1910		1911	
	Kilos	Lire	Kilos	Lire
c) Reggio (Calabria):				
North German Ports	—	—	—	—
Austria-Hungary	11 214	224 280	10 345	258 625
France	26 297	525 940	27 076	676 900
United Kingdom	2 417	48 340	1 733	43 325
Netherlands	—	—	—	—
U. S. of America	36 210	724 200	26 774	669 350
Other countries	741	14 820	555	13 875
Total	76 879	1 537 580	66 483	1 662 075

d) Palermo:				
North German Ports	3 048	45 720	2 840	56 800
Austria-Hungary	32 694	490 410	30 760	615 200
Belgium	2 321	34 815	2 150	43 000
Denmark	265	3 975	220	4 400
France	15 597	233 955	12 345	246 900
Greece	61	915	—	—
United Kingdom	50 331	754 965	48 235	964 700
Netherlands	610	9 150	720	14 400
Russia	240	3 600	265	5 300
Sweden	—	—	—	—
Norway	—	—	—	—
Spain and Portugal	615	9 225	415	8 300
Turkey	30	450	40	800
U. S. of America	15 999	239 985	12 785	255 700
South America	—	—	—	—
Australia	3 480	52 200	3 260	65 200
Egypt	135	2 025	—	—
India	—	—	—	—
Italy	—	—	—	—
Other countries	—	—	—	—
Total	125 426	1 881 390	114 035	2 280 700

Total exports 1911.

Port of shipment	1910		1911	
	Kilos	Lire	Kilos	Lire
Messina	175 816	3 516 320	457 714	9 154 280
Catania	251 776	5 035 520	129 141	2 582 820
Reggio (Calabria)	76 879	1 537 580	66 483	1 662 075
Palermo	125 426	1 881 390	114 035	2 280 700
Total	629 897	11 970 810	767 373	15 679 875

1911	Kilos	767 373	Lire	15 679 875
1910	"	629 897	"	11 970 810
1911 increase	Kilos	137 476	Lire	3 709 065

profit, hence at about the middle of October the first sales for delivery were made at these figures.

As soon as the ice was broken and a definite rate of value had been established for the new oil, a large French firm, through its local agent, set about to buy up every parcel of oil for delivery which came into the market, and continued to buy, even at rising prices, until it had secured a supply of about 15 000 kilos.

As a result of this the prices for delivery were rushed up from 41 *M* to about 46 *M*, and they stood at that height when the first new oil came into the market. As is well-known, the ester-content of bergamot oil depends upon the degree of maturity of the fruit. Unripe fruit yields an oil containing between 28 and 32% linalyl acetate; riper and wholly-mature fruit produces an oil of which the ester-content may reach a maximum of from 42 to 44%.

As the standard of value of bergamot oil is its linalyl acetate content, it used, in previous years, to be in the interest of the manufacturer to begin to work up his fruit only when it had reached full maturity. But in the present season the high prices paid for old oil and the strong demand from foreign countries which, for lack of old material, were content to take low-grade new oil, induced the manufacturers to work up their bergamot fruit in a less mature state than formerly, especially in view of the fact that when the fruit is comparatively green its percentage of ester is generally greater than afterwards.

In the past, when the crop was abundant, the consumers were in the habit of preferring high-grade expensive oils to the cheaper low-grade qualities, but this season, owing to the old stocks having been exhausted, there were plenty of buyers who were prepared to accept oils of a low standard.

The result was that in the month of December a period of great activity set in in the bergamot oil market, during which the manufacturers were able to dispose readily of their new oil at prices ranging from 43 to 48 *M*. All the signs pointed to a further continuation of regular conditions of sale during the manufacturing-season when, in the first days of January, a natural catastrophe upset all previous calculations and estimates.

Violent whirlwinds of a typhoon-like character afflicted the Calabrian coasts on January 3rd and 4th, and again on January 6th and 7th. So great was the force of the storm that almost the whole of the fruit which remained on the trees was blown down, only a few favoured valleys being saved from the havoc of the elements. In many localities not only was the fruit blown down, but hundreds, if not thousands of trees were uprooted.

It is a familiar fact that the preparation of bergamot oil is a difficult and irksome task, for which appropriate mechanical appliances are necessary. Now, in the short interval which elapses between the falling of the fruit

and the time when, damaged by its fall, it begins to rot, it was impossible to work up the enormous mass of windfalls into oil; the more so because owing to emigration to America there is a constant want of labour in Southern Italy, and there are no means of increasing the available number of hands during the manufacturing season. Hence the oil of many thousands of bergamots has gone to waste, and even the fruit which it was found possible to work up yielded scarcely one-half of an average oil-output, owing to the peel having been injured by the fall. The storms described above have therefore proved a terrible scourge for the fertile districts of Calabria, inflicting serious damage upon most of the manufacturers and causing great financial losses. Another result of the climatic disturbance was that the fruit which had previously been on the trees, almost all in an immature condition, was prevented from ripening and that such oil as was prepared from the windfalls was therefore without exception of a low grade. It may be taken for granted that at least one-half of the crop has had to be worked up in this summary manner and under these unfavourable conditions in the month of January, and that the shortage of oil as compared with the previous estimates may be put as at least 30 to 40%.

It goes without saying that these events brought the manufacturing season to a sudden, premature close, and the consequences of the unfavourable conditions which have prevailed may be summarised in the statement that the crop has yielded barely more than 40 to 45% of a fair average output, and that almost without exception the oil produced is of a very low ester-content. Oils of 37 to 38% ester-content are scarce and only to be found in very small quantities.

It is quite natural that under such disastrous circumstances the market has been subject to unusual fluctuations. On the one hand the manufacturers, without exception, have produced at most one-half of the quantity of oil they had expected to make, on the other the oil produced is of a lower grade than that which they themselves had made contracts to deliver. They have therefore suffered damage in two different ways, and many of them have been unable to observe their obligations towards the exporters. The latter, again, finding that they could not depend upon receiving all the oil they had contracted for, and which they needed to cover their own sales, found themselves compelled to buy elsewhere to cover their requirements, and this state of things led to a wild rushing up of prices, in the course of which the article was forced up within a few weeks from *ℳ* 45.— to *ℳ* 46.— to a parity of *ℳ* 65.—, heavy sacrifices being exacted from the exporters.

Is it surprising, in the circumstances described above, that the sorely-tried manufacturers should now stubbornly insist upon these high prices, in order that the profit upon the small lots of oil still in their possession may help somewhat to alleviate the wounds that have been inflicted upon

them? On the other hand, who shall blame the consumer who, face to face with such quotations, grows more and more chary of buying such an expensive article as bergamot oil, and steadily more inclined to extend friendly consideration to the artificial oils of commerce?

For the reasons above described there is very little satisfaction to be derived at present from the bergamot oil business. The exporter, who is confronted with great difficulties in his dealings with customers abroad and who is responsible for the quality of his shipments, has very little inducement nowadays to continue trading in an article in which the opportunities for making profit no longer stand in just relation to the chances of losing money. It only remains to be hoped that in the future better crops will bring about an improvement in the market-position, and that the trade in this fine article of commerce may then regain the interest which for the present it has lost in the eyes of all concerned in it.

Within the past few weeks the oil-prices have given way slightly because in a few isolated instances manufacturers have attempted to realize, but there is a total absence of any desire to buy. The present buying-price of the oil ranges from *M* 60.— to *M* 63.—.

Special stress should be laid upon the fact that oil produced under such unfavourable and abnormal conditions as those of the present season is no match for the product of previous crops, either in respect of quality or of physical constants. Speaking generally, the odour of the present season's oil leaves as much to be desired as do its ester-content, its rotatory power and its specific gravity. As all the oil has been prepared from more or less immature fruit, the low ester content goes together with a very low sp. gr. and an abnormally high rotation, reaching $+2^\circ$ and 23° in the case of some few samples.

Lemon Oil. This important article has undergone numerous and no unimportant fluctuations in the course of the last seven months. The last crop, as is well-known, had yielded only a poor medium result, while at the commencement of the 1910/1911 season there was a very heavy stock of old oil on hand. The old supplies have served to eke out the deficiencies in the more recent output, and throughout the season there has been an abundant supply available to meet the requirements of the export-trade. In the last Report the causes which, in spite of this plentiful supply, caused the article to advance at the beginning of September to the high level of from *M* 14.50 to *M* 15.— were set forth in detail. Right from the beginning of the present crop opinions have been divided on the subject of its size: the majority of those interested judging it with great optimism, while others declared it to be smaller than the previous crop. Under the influence of these contradictory views a downward tendency declared itself in Messina in the autumn, which strongly affected the prices, both of spot-supplies and of oil for delivery. The

local exporters vied with each other in offering new oil for delivery to customers abroad at lower and lower rates, while the owners of spot oil in Messina tried their best to rid themselves of the stocks in their warehouses.

Local speculators likewise took a hand in the slump, which, however, was in no wise justified by the statistical position of the article, and between the beginning of September and the end of October the price of oil for prompt delivery was depressed from *M* 15.— to *M* 12.—, and that of oil for delivery from *M* 11.— to *M* 10.50. This movement had for its result to make foreign buyers very reticent of buying oil for prompt delivery, and to keep them from giving even to the low prices of oil for delivery the attention which they merited on the intrinsic strength of the situation. It was only, so to speak, on the threshold of the new crop, that is to say when in the month of November the first large shipments of boxed fruit were being shipped abroad, that a view began to spring up that the quantity of fruit on the trees had been generally largely over-estimated, and that in the most favourable case the new crop would only equal that of the previous year.

The spread of this conviction put a stop to the decline of the market, and at this juncture, of course, the upward reaction began to make itself felt, with the result that within a few days' time new oil for delivery had risen to *M* 10.75. In the beginning of December it had further advanced to *M* 11.—, and until the arrival on the market of the new oil from *M* 12.25 to *M* 12.50 was being paid for available old lemon oil.

In the meantime, the slump during the months of September and October had resulted in local speculators and exporters being caught with large uncovered sales, and when the first deliveries fell due in the month of December both the exporters and the local contractors called for larger quantities of oil than the manufacturers were able to supply.

Whereas in the previous year, at the beginning of the season 1910/1911, there was a balance of over 100 000 kilos of old oil at the disposal of the export-trade, barely 30 000 kilos of old stock was found to be similarly available in December 1911. This scarcity of oil caused a slow tightening of the prices, which recovered to *M* 11.50 in the first half of January.

Early in the second half of January the East- and North-coasts of Sicily were visited by severe gales, which caused enormous quantities of lemons to fall, and also worked serious havoc among the trees. The quantity of fallen fruit was so large that, in order not to lose the whole, a portion of it was used only for the manufacture of citrate of lime, and the idea of working up the fruit for essential oil was given up. This meant a not inconsiderable shortage in the production of lemon oil, and afforded a fresh excuse for advances in the quotations. The price rose rapidly by leaps and bounds to *M* 12.50 at the beginning of February,

and to *M* 14.25 in the course of the first half of that month. After remaining steady at that figure there was a fresh upward rush early in March to *M* 14.85, the highest price paid during the present season.

Lemon oil therefore has now regained the level of price at which it stood last September, and there is hardly any room for doubt that the upward tendency would have continued, if the threatened coal-strike in England had not cast its shadow before, chilling the assurance of the bull-party and encouraging the hopes of the numerous section of those traders, both in Sicily and abroad, who had been caught bare of supplies. As a result of the strike, which had broken out in the meantime, the price of lemon oil gave way to the extent of about 0,50 *M*, and at the time of writing it stands at 14,25 *M*. It is extraordinarily difficult, this season, to find an answer to the question what will be the future course of the lemon oil market, a question which everyone interested in the article is asking himself.

The statistical returns indicate that, putting it at the highest, the production available for the world's consumption will not exceed that of last year, while it must not be overlooked that in that year the world's requirements not only absorbed the whole of the current crop, but 70000 kilos of old stock in addition. The shipments during the last three months of the present season exceed by 50000 kilos those of the corresponding period of last year, and it is evident that the 30000 kilos or so which were left in stock from the last crop must have gone into consumption, as there has not been enough new oil available to account for the export of such large quantities. During these three months no supplies of new oil worth mentioning can have accumulated here; even at the present time, when three-fourths of the manufacturing season is over, the trade is living from hand to mouth; the manufacturers are in arrears with their deliveries, and several large export firms have only imperfectly fulfilled their delivery-contracts. In the district of Palermo the conditions of the lemon-oil industry appear to be particularly bad this year, for the lemon crop there has been even scantier than in the other parts of Sicily, and a large part of the inferior fruit is being forwarded thence, packed loosely in railway-trucks, to the large cities of Upper Italy for alimentary purposes. Moreover, up to the present the lemon-oil manufacturing industry in the district is not yet in full swing, and is hardly likely to be so this year, for in spite of the high oil-prices the growers are able to obtain better returns by selling their fruit for human consumption in the home-market. The only cause which could conceivably bring about a considerable decline in the oil-prices would be an accumulation of large stocks, and so far there are no indications of any sort pointing to the possibility of such an accumulation either in the near or more distant future. Again, it would appear that foreign countries have not yet laid in the whole of their annual requirements. It seems fair to assume that in these circumstances or

a complete stagnation in the world's trade, whether resulting from war or other causes, can bring about a considerable decline of the lemon oil prices in the coming summer. But so far as can be foreseen there is no prospect of any serious depression in the world's trade. For these reasons there seems to be very little chance of any important decline in the prices just yet, while a continuation of the present level of quotations and the possibility of higher rates appear to be more likely to be realized.

With regard to the prospects of the next crop it is impossible at the present time even to hazard a prognostication. Throughout Southern Italy the winter has been exceptionally mild; the rainfall has been slight, and there has scarcely been any snow lying in the mountains. Owing to the mildness of the weather all trees of the *Citrus* species, with the exception of the bergamot trees, have developed an abundant foliage, by which the favourable development of the blossoms is made possible, but the scarcity of rain and snow and the dryness of the subsoil which is even now noticeable, are disturbing factors which neutralise the hopes mentioned above. The real conditions will only become clear as the spring advances and confirms either the hopes or the fears for the coming crops.

Special reference should be made to the appearance of the so-called blood-lice of the shield-lice species, a pest which within the last two years has visited extensive districts, especially in the immediate neighbourhood of the larger towns of Sicily and Calabria, attacking all the trees of the *Citrus* species and gradually killing them. Mandarin-, bergamot- and lemon-trees appear to be specially liable to the attacks of this pest; the sweet- and bitter-orange trees seem to be better able to resist it. Systematic experiments conducted by the State Schools of Agriculture appear to have resulted in the discovery of suitable antidotes. Unfortunately the remedies which have so far been suggested, all of which consist in the repeated spraying of the whole tree with some insect-killing liquid, are not only difficult of application but considerably increase the cost of cultivation without guaranteeing a cure. This new disease of the *Citrus* trees certainly constitutes a serious danger to our horticulture and to the essential oil industry of Sicily and Calabria. It is to be hoped that Science will soon discover means of conquering and destroying this new pest.

Mandarin Oil. This year's mandarin crop has been of fair average quantity. Nevertheless, from the commencement of the season, the prices of mandarin oil have been higher than might have been expected and have maintained a steady level almost without fluctuations. The reason of this is the entire absence of old stock, both here and abroad, which enabled the new oil to find a favourable market at the outset, a condition which is still maintained.

Orange Oil, Bitter. In September 1911 the price of last year's bitter orange oil stood at 16 *M*, and as the new crop, in common with that of

sweet oranges, was not a good one, the price of the oil advanced slowly in the course of the winter. There has been no chance for stocks of any importance to accumulate and it is therefore possible that consumers will have to pay higher rates in the future. Generally speaking it would seem that in the course of the last few years the interest in this article had declined.

Orange Oil, Sweet. When the new crop arrived the market was wholly bare of supplies. Hence, immediately upon the arrival of the new oil a brisk turnover ensued, which became all the more animated because the orange crop was known to be small. In sympathy with these conditions the oil-prices, from the beginning of the season, showed a slight upward tendency from 17 *M* to about 18 *M*. Business only slackened somewhat when some little stock had again accumulated here and where buyers abroad were able to dispose of their shipments, recently-arrived and afloat. Those with expert-knowledge of the market improved the occasion by taking advantage of the receding prices and by buying in the falling market. At last, about Christmas-time, prices reached their lowest ebb and since then, rising by slow degrees, they have again reached a parity of 18 *M*. The stocks of orange oil are very small and it is more probable that higher prices will rule during the summer months.

Preparation of the Oils of the Agrumi.

It is common knowledge that the oils of the *agrumi* are prepared by expression from the peel. Frequent attempts have been made to find another method of manufacture, but so far without success. The advantage of the present process is that the oil which is gained by expression from the peel conserves in its entirety its pure natural aroma, whereas ordinary steam-distillation (under atmospheric pressure), yields an oil possessing a different odour and of inferior quality. On the other hand the disadvantage of the expression-process is that it requires much human labour. A further, and in our view a still greater, drawback is that this process leads to the waste of enormous quantities of oil, for it is obvious that by expressing the oil from the peel into a sponge, and again squeezing it out of the sponge into a vessel, only a portion of the oil expressed, and probably only the smaller portion, is actually gained.

The subject is one of not inconsiderable financial importance for Italy. The average annual exports of the oils in question from 1899 to 1908 inclusive amounted to 934 952 kilos, representing a value of 15 350 737 Lire. In 1909 and 1910 they were smaller: 629 897 kilos (value 11 970 810 Lire) in the former and 604 299 kilos (value 11 676 575 Lire) in the latter year.

¹⁾ Report April 1910, 48.

In some, but probably only isolated, instances, attempts are made to reduce the loss in handling by distilling the expressed peel with water, but, as stated, this method only yields an inferior oil.

Recently, however, Patané and Carelli¹⁾ have published a report on a new method of working-up lemons which has been proposed by Professors Peratoner and Scarlata. This process has been patented by the two Professors and is published as an essay in the competition for the prizes offered by the *Agrumi*-industry for the best solution of the problem. It consists in cutting up the lemons into small pieces, and pressing them so thoroughly that the juice, in exuding, carries with it the oil which is liberated by the bursting of the cells in the peel. The acid liquid is then subjected to distillation under diminished pressure at a distilling-temperature not exceeding 60°. The distillation-residue from which the oil has been removed is worked-up for lemon-juice.

Professors Patané and Carelli have applied their process experimentally at the Chemico-Pharmaceutical Institute of the University of Palermo, and have compared the results obtained by them with those which they obtained by hand-pressure by the old method. Parallel-tests yielded, by distillation 0,12 and 0,136%; by hand-pressure 0,115 and 0,16%. So far as the yield is concerned there is therefore no very marked difference between the two methods.

The idea of working at a low distilling-temperature is quite correct, for when the oil evaporates between 50 and 60°, a temperature at which not even the albumen in the cells coagulates, the distillate preserves the pure aroma of the fruit. There will of course remain a slight, although perceptible difference between the odour of this oil and that which has been obtained by pressure, because the expressed oil contains several per cent of non-volatile waxy substances in solution, which temper the sharpness of the aroma.

Being familiar with the injurious influence of high temperatures upon the oils in question, we have for many years past only rectified lemon oil, orange oil, and bergamot oil at the low temperature of 40 and about 50°.

One objection, however, we must be allowed to make against the process of Peratoner and Scarlata: the yield of oil is too low. In our view it is a matter of prime necessity that, even if perhaps not all the existing oil is recovered, at any rate the yield should be materially higher than it is in the hand-pressing process which is now customary. On the other hand the simplification of the process, although it may also be useful, is of decidedly secondary importance.

With a view of obtaining positive information on the possibility of an increased yield we have procured a large quantity of freshly-gathered

¹⁾ Bollettino del Ministero di Agricoltura, Industria e Commercio. Anno IX, Serie C, fascicolo 9, p. 21.

lemons, with which we have made several experiments in distilling. We relate below the result of our experience with that method of manipulation only which produced the best results: —

The yellow layer of the peel, which contains the essential oil of the lemon, is removed by peeling. The thin peel which is thus obtained is shredded and bruised mechanically as small as possible. The oily paste is liberally diluted with water and the resulting thin mass is distilled without previous expression, at between 50 and 60 mm. pressure, until the distillate contains not a drop more of oil. All indirect heating with steam-jacket vapour during the distillation must be avoided, and only steam of any desired pressure which passes directly into the liquid should be used. It is not necessary to cohobate the resulting water of distillation; it may be used instead to dilute the paste in the next distilling-operation.

By this process we obtained from the lemons 0,3% by weight of oil with a pure odour, possessing the following properties: —

$d_{15^{\circ}} 0,8551$, $\alpha_D + 55^{\circ} 30'$ (α_D of the initial 10% of the distillate $+ 48^{\circ}$
citral 3,4%.

$d_{15^{\circ}} 0,8547$, $\alpha_D + 56^{\circ} 22'$ (α_D of the initial 10% of the distillate $+ 50^{\circ} 4'$
citral 4,5%.

The higher the distilling-temperature maintained, the more favourable is the course of the distillation, and the easier it is to increase the output, but at the same time the more the aroma of the oil suffers. On the other hand, a low temperature ensures the purity of odour of the oil, but it also renders the evaporation more difficult, with the result that a small proportion of oil, and especially of the less volatile citral, distils over. The most favourable temperature is perhaps about 50° , or (when the temperature of the condensing-water is over 20°) nearer 60° .

Care should be taken to render the distilling apparatus, the condensers and the receivers, as nearly air-tight as possible in order to prevent the air-pump from sucking up too much air through the apparatus, and thus to cause the wastage of oil by volatilisation. For it must be remembered that every gallon of this air is also charged with a gallon of oily vapour saturated at the temperature of the water of condensation, and that the oily vapour is lost.

Owing to the low distilling-temperature the cell-walls of the raw material inside the still retain their natural turgescence for some little time, a circumstance which greatly retards the liberation of the oil from closed cells; hence it is absolutely necessary to disintegrate the peel thoroughly that every cell is opened.

A yield of 0,3% equals more than twice that obtained by hand-pressing. We believe, however, that with some experience it will be possible to increase still further the output of oil by our process. With water-distillation under diminished pressure the less volatile constituents, especially

when they are to some extent soluble in water, may easily escape evaporation. In the case at issue the valuable citral would thereby be primarily affected. It is certain that at 50° only a very small proportion of the citral which has been dissolved in the water will evaporate. Therefore, too much water must not be used in diluting the peel-pulp. On the other hand it is necessary that the boiling mass inside the still should preserve a certain degree of fluidity in order that the inflowing steam may set up an undulating motion in it. For this reason we only distilled the thin upper layer of the peel, and not the entire peel — which would have been simpler and less laborious —, because if the entire peel had been used the increased mass of distilling-material would have required the addition of a far larger proportion of water and would thus have kept more citral in captivity.

Possibly the above particulars may contain some useful hints for the improvement of the Italian *agrumi*-industry, but we feel it necessary to call attention to another very characteristic difference between distilled oil and hand-pressed oil.

It is common knowledge that oils of lemon and orange can only be kept in good condition for a very limited period, and that after some time they acquire a foreign, acrid odour. If they have been kept in a corked bottle, it will be found that the cork has been bleached pale yellow. Protected from light and air the hand-pressed oils, owing to their wax-like constituents, may be kept for more than a year, but not for several years. It is different with the wax-free distilled oils; their keeping power is much smaller. When the distillation has been conducted under atmospheric pressure by means of water, that is to say at about 100° , the oil begins to deteriorate after some weeks, or a few months. Oils of lemon and orange which have been distilled at about 50° retain their pure odour for a longer period, but, according to our experience, scarcely as long as twelve months.

Bergamot Oil. In the table below we present a symposium of the characters of a series of bergamot oils which have been submitted for our opinion within the past six months and which have proved to be adulterated.

Samples Nos. 1 to 5 contained added terpinyl acetate, in proportions varying from 14% in No. 1 to about 3% in No. 5. With the exception of the sp. gr. of No. 1, which was too high, the constants of the samples were generally within the limits of the values for pure bergamot oils; hence the adulteration was only demonstrable after fractional saponification. Sample No. 6 was also suspected of containing added terpinyl acetate; and moreover, contained an ester belonging to the group of esters of sparingly soluble acids, the saponification value of the evaporation-residue and the difference between saponification value and acid value II being

not inconsiderably in excess of the limits of value of pure bergamot oil. It was however impossible to carry out a more detailed examination of this oil, or to identify the ester in question, owing to the insufficiency of the sample submitted.

The altogether abnormal constants of sample No. 7 at once showed it to be adulterated, and even gave rise to the suspicion that it represented not so much a grossly-adulterated oil as an altogether worthless artificial product.

Sample No.	1	2	3	4	5	6	7	8
d_{15}^0	0,8967	0,8867	0,8833	0,8853	0,8833	0,8795	0,8781	0,8845
α_D	+21° 12'	+19° 14'	+18° 0'	+18° 25'	+16° 55'	+23° 16'	+54° 40'	+16° 40'
Evap. Residue	6,5%	4,0%	5,0%	6,4%	4,8%	4,8%	4,8%	5,6%
Sap. v. of evap. res. . .	192,5	182,1	170,2	182,0	175,0	221,7	332,4	185,0
Sol. in 90% alcohol . . .	0,5 vols. a. m.	0,3 vols. a. m.	0,3 vols. a. m.	0,4 vols. a. m.	0,3 vols. a. m.	0,5 vols. a. m.	—	0,2 vols. a. m.
Acid v.	2,9	1,6	1,5	2,2	1,5	1,2	0,9	1,8
Ester v. after 1 h. sapon. with 10 cc. seminorm. sol.	99,5	105,7	96,9	101,8	95,0	100,7	—	100,8
Ester-content (calc. as linalyl acetate)	34,8%	37,0%	33,9%	35,6%	33,2%	35,2%	—	35,3%
Ester v. after 2 h. sapon. with 20 cc. seminorm. sol.	111,9	114,1	101,6	106,5	98,7	102,9	76,0	103,9
Ester v. after 1 h. sapon. with 10 cc. seminorm. sol. + 25 cc. alcohol .	87,5	97,7	90,8	97,1	90,7	97,7	61,1	97,5
Difference	24,4	16,4	10,8	9,4	8,0	5,2	14,9	6,4
Sap. v.	102,0	107,3	98,4	104,0	96,5	101,9	62,0	102,6
Acid v. II	91,2	101,0	90,9	97,1	89,8	89,6	52,3	96,4
Difference	10,8	6,3	7,5	6,9	6,7	12,3	9,7	6,2
Terpenyl acetate content, about:	14%	8%	4%	3,5%	3%	suspect	7%	suspect
Esters of sparingly sol- uble acids	Not demonstrable					present	not demonstr.	not demonstr.
Glycerol esters	Not demonstrable					not demonstr.	"	about 1%

Sample No. 8 contained about 1% glycerol ester and probably, in addition thereto, a small quantity of terpinyl acetate. After having been shaken four times with an equal volume of 50% alcohol (Report April 1911, 150) it was found that the weight had decreased down to 33,6% of the original. Evaporation of the four solutions of the glycerol ester and subsequent fractional distillation *in vacuo* yielded a few grms. of the ester boiling between 125 and 130° (4 mm.), with the following constants: d_{15}^0 1,1564, $\alpha_D \pm 0^\circ$, n_{D20}^0 1,44317, acid v. 2,8, ester v. 610,6, sol. in about 5 vols. water and more. Estimation of the constituents of the ester showed about 39% glycerol and 64% acetic acid.

In connection with the above we submit the constants of a few samples of bergamot oil in which no foreign esters were detected, but of which

the properties are nevertheless recorded here for the purpose of showing what low-grade products are placed upon the market as the result of the present high price of bergamot oil: —

d_{15}^0	0,8812	0,8802	0,8667	0,8710	0,8694	0,8629
α_D	+ 22°	+ 19° 35'	+ 56° 30'	+ 30°	+ 30° 40'	+ 53° 50'
Residue of evap.	4,5%	4,4%	3,2%	—	—	1,7%
Solub. in 90% alcohol	0,2 vols. a. m.	0,2 vols. a. m.	0,5 vols. a. m.	10 vols. insoluble	10 vols. insoluble	4,5 vols. a. m.
Acid v.	1,6	2,8	1,5	1,8	1,8	0,9
Ester v.	76,9	76,5	57,7	45,7	36,4	41,1
Ester (calc. as linalyl acetate)	26,9%	26,8%	20,2%	16,0%	12,7%	14,4%

Lemon Oil. In our Report of November 1908 (p. 61) we stated that in the examination of a considerable number of samples of authentic lemon oils we had estimated the citral-content by a method which had been communicated to us from a friendly quarter (Dr. Kleber), but which so far had not been published. Comparative tests with mixtures of known citral-content, made at the time, demonstrated the satisfactory character of the method. We ascertained the citral-content of the lemon oils in question to be from 4,3 to 7,2%. Afterwards (Report October 1911, p. 45) we made it known that in its original form the method had given values which, in part, were found to be too high, and that after having improved the method it only showed a citral-content of from 4 to 5%.

We are glad that, after a long interval, the publication of a paper by Kleber¹⁾ enables us to give further particulars of the method, and our satisfaction is the greater because expressions of criticism of our prolonged silence have already made themselves heard²⁾. As however, the method was made known to us in confidence by Dr. Kleber at the time, we did not regard ourselves entitled to publish it. The basis of Kleber's method is the observation that phenylhydrazine (when di-ethyl orange is used as an indicator) gives a sensitive titration with mineral acids, and that with aldehydes and ketones it forms hydrazones which give a neutral reaction with di-ethyl orange. Kleber proceeds as follows: —

About 10 g. lemon oil are exactly weighed into a flask, 20 cc. of freshly-prepared 5% alcoholic phenylhydrazine solution are added, the stoppered flask is allowed to stand about half an hour at about 35°, after which as much seminormal hydrochloric acid is added as is required to neutralise the phenylhydrazine solution, the quantity having been previously estimated by a separate test. The mixture is poured into a separator, the flask itself rinsed out with 20 cc. water and the whole vigorously shaken. As soon as the two layers have separated, the lower of the two is drawn off into an titration flask, the residue washed out with

¹⁾ Americ. Perfumer 6 (1912), 284.

²⁾ Umney, Perfum. and Essent. Oil Record 2 (1911), 260.

5 cc. water and added after separation of the solution previously run off and the total contents of the flask titrated with seminormal soda liquor. Di-ethyl orange is used as an indicator and in all cases the titration is made for the brownish tint which precedes the pink coloration. As each cc. of seminormal soda liquor corresponds to 0,076 g. of citral, the citral content of the oil may be calculated from the amount of soda liquor which has been used up.

Kleber found that parallel-tests almost invariably produced exactly corresponding results, and that in the case of mixtures of known composition the difference rarely exceeded 0,1%. As the phenylhydrazine solution decomposes very rapidly, it is best prepared fresh each time; and in no case should a solution be employed which is more than 24 hours old. If necessary, the phenylhydrazine should be rectified beforehand *in vacuo*.

Kleber has ascertained that his method is also suitable for estimating the citronellal-content of citronella oil, and that it may be specially employed with advantage in the evaluation of Java citronella oil. He found Ceylon citronella oils to contain from about 7 to 9%, and Java oils from about 32 to 37% citronellal, but in view of the limited number of estimations which have thus far been carried out these figures are of course not to be taken as limits of value¹). Kleber uses 5 g. Ceylon oil or 2 g. Java oil in his determinations.

Kleber believes that his method may be found generally applicable for the estimation of aldehydes and ketones and leaves it open to his colleagues in research-chemistry to make further experiments in this direction.

We have already stated that Dr. Kleber communicated his method to us privately some considerable time ago and that, as our own experience has shown it to give really practicable results, we are able to recommend it. We ourselves have somewhat modified the method and proceed as follows:—

About 2 cc. oil are mixed with 10 cc. of a freshly-prepared 2% alcoholic phenylhydrazine solution, and allowed to remain undisturbed during 1 hour in a glass-stoppered flask of about 50 cc. capacity. We then add 20 cc. decinormal hydrochloric acid and mix the liquid by gently moving the flask backwards and forwards. After adding 10 cc. benzene the mixture is shaken vigorously and poured into a separating funnel. The acid layer, amounting to about 30 cc., which separates out clearly after the mixture has been left to settle a short time is then filtered in a small filter.

To 20 cc. of this filtrate 10 drops di-ethyl-orange solution (1 : 2000) are added and the mixture is titrated with decinormal potash liquor until a distinct yellow colour appears. From this the quantity, in cc., of deci-

¹) We ourselves have previously found a higher citronellal-content in both these oils by an indirect method of estimation. Further examinations are needed to clear up these contradictory results (Report October 1899, 21, and April 1900, 14).

normal potash liquor required for 30 cc. of the filtrate is calculated. For the purpose of estimating the value of the phenylhydrazine solution a blank test without oil is made in a similar manner. If it is found that the quantity of decinormal potash liquor used up for 30 cc., of the filtrate = a in the first, and = b in the second experiment, it follows that the quantity of citral present in the amount of oil under test (s grms.) equals $a - b$ cc. of decinormal potash liquor. Hence, 1 cc. decinormal potash liquor being equal to 0,0152 g citral, the percentage proportion of citral in the oil is expressed by the following formula

$$\frac{(a - b) \cdot 1,52}{s}$$

The object of the extraction with benzene (in which we have followed a suggestion of Kleber) is to re-clarify the solution, which becomes turbid after the addition of the hydrochloric acid. We have observed that when this has been done it is easier to recognise the change in the colour during the titration.

We summarise below the results which we have obtained by this method with mixtures of known citral-content. These figures clearly show the usefulness of the method.

		Percentage of the solution			
		2%	4%	6%	7,3%
Found	{	2,4%	4,1 %	6,2 %	6,9 %
		2,0%	4,0 %	5,9 %	7,0 %
		—	3,9 %	6,0 %	7,1 %

From a paper by Chace¹⁾ we observe that several American chemists have also obtained satisfactory results with Kleber's process. Comparative determinations by the methods of Chace (Report April 1907, 116), Hiltner (Report October 1910, 163), A. H. Bennett (Report April 1909, 110, October 1909, 153) and Kleber have shown that the last-mentioned method not only appears to afford the best results, but is also the easiest to carry out. The least satisfactory of all were the colorimetric tests; Hiltner's method regularly gave results below the actual values, Chace's, above them. In respect of accuracy of results Bennett's method came next to Kleber's, but Bennett's method failed partly in this particular that not all the chemists who applied it were able to recognise beyond a doubt the concluding point of the reaction.

As a result of the experiences set forth above the official chemists of the Bureau of Agriculture of the United States, at their 27th Annual Meeting, agreed to recommend Kleber's method for the determination

¹⁾ U. S. Dep. of Agriculture, Bureau of Chemistry. Bulletin No. 137 (20. VII. 1911), p. 64.

of citral in oils of lemon and orange. In addition to this they propose the colorimetric method of Hiltner¹⁾. The citral-content test of orange oil has for its principal object the detection of any added citral or oil of lemon. If the citral-content ascertained by Hiltner's method exceeds 0,7% such an adulteration is probable.

J. R. Rippetoe and L. E. Wise²⁾ have also been working at the estimation of citral in oils of lemon. Their reason for taking up this investigation was the desire to substitute another and more reliable method for that of Sadtler (comp. Report April 1904, 48 and October 1904, 119) which has been incorporated in the U. S. Pharmacopœia. With this object in view they submitted the methods worked out by Chace and Hiltner to control tests, and they came to the conclusion that Hiltner's method might possibly be suitable for admission into the Pharmacopœia. In that case, of course the minimum-content of citral demanded by the Pharmacopœia would need to be reduced from 4 to about 3,8%.

Parry³⁾ reports on several shipments of lemon oil adulterated with turpentine oil. The oils in question were distinguished by their abnormally low optical rotation ($+50$ to $+54^\circ$), and also attracted Parry's attention because their citral value was very low (3,3 to 4,1%). Closer examination revealed the presence of copious quantities of pinene, pointing to sophistication with turpentine oil. The comparatively small drop in optical rotation considering the amount of adulterant present leads Parry to think that in every case the adulterant was Greek turpentine oil, which has a high dextro rotation, and he was confirmed in this view by hearing from Sicily that Greek turpentine oil is used there as an adulterant of lemon oil.

Orange Oil. According to Brooks⁴⁾ it would be possible to prepare in the Philippine Islands from the peel of the fruit of *Citrus reticulata* Blanco, known locally as *naranjita*, an oil which is almost identical with Italian orange oil. *Citrus reticulata* is generally regarded as being synonymous with *C. Aurantium*, L., but Brooks is of opinion that this is not correct. The oil, which was pressed from the green peel, had the following constants: $\alpha_{D30} 90,85^\circ (+?)$, $n_{D30} 1,4700$, ester v. 8,0, residue of evaporation 2,2 to 2,4%. It contained about 92% limonene, about 0,3% of a wax-like stearoptene, m. p. 116 to 117°, 0,5% of an acid (possibly butyric or caprylic acid), and traces of a phenol.

Another *Citrus*-species which is cultivated in the Philippines is *Citrus Aurantium*, Blanco, the fruit of which is locally known as *cajel*. This fruit

¹⁾ Hiltner now uses for purposes of estimation 5 g. oil. U. S. Dep. of Agriculture, Bureau of Chemistry. Bulletin No. 137 (20. VII. 1911), p. 72.

²⁾ Americ. Journ. Pharm. 83 (1911), 558.

³⁾ Perfum. and Essent. Oil Record 2 (1911), 209.

⁴⁾ Philippine Journ. of Sc. 6, A. (1911), 345.

is not suited for the preparation of oil, the yield being too small. The constants of the oil are as follow: $d_{40}^{30} 0,8390$, $n_D 1,4675$, sap. v. 8,5.

The precise botanical classification of the two *Citrus*-species still remains to be determined.

Eucalyptus Oil. There is very little to be said concerning this oil, the market position having undergone hardly any change. Lately, however, the demand for the common Australian variety, which consists chiefly of "amygdalina" oil, has been so keen as to lead to a tightening of prices, but whether the present range of values can be maintained remains to be seen. "Globulus" oil has also been in strong demand, but the chief interest continues to be manifested in our pure eucalyptol, which we are in a position to supply on most favourable terms.

The enormous quantities of eucalyptus oil which have lately been used in the mining districts of Australia in the recovery of zinc and lead sulphides¹⁾, have induced Mr H. G. Smith the well-known chemist, to enquire whether the Australian Commonwealth will be able to continue to supply sufficient oil to meet the demand²⁾. At present the gathering of the leaves is still too costly, and moreover the necessary hands for the work are lacking, but Smith is of opinion that this difficulty may be overcome by the use of machines for collecting the raw material, and by the erection of large plant. Generally speaking, he says, the distilling plants are much too small; he has only seen one still (on Kangaroo Island) capable of holding 5000 lbs. of green leaves (of *Eucalyptus cneorifolia*). The charge from this still can be emptied within 6 minutes, and each distillation yields about 100 lbs. oil. If heating by open hearths were replaced by steam-heating it would be possible, according to Smith, considerably to increase the yield.

We cannot spare the space to refer in detail to the enquiries made by Smith in the different districts, but his report clearly shows that at present the distillation of eucalyptus oil in Australia is not yet conducted on rational principles.

The third part of the second volume of J. H. Maiden's work entitled "A critical Revision of the Genus *Eucalyptus*"³⁾ contains a description of the following *Eucalyptus*-species: *Eucalyptus affinis*, Deane et Maiden, *E. paniculata*, Sm., *E. polyanthemos*, Schauer (*E. Dawsoni*, R. T. Baker; *E. polyanthemos*, Schauer var. *glauca*, R. T. Baker; *E. ovalifolia*, R. T. Baker; *E. ovalifolia*, R. T. Baker var. *lanceolata*, R. T. Baker et H. G. Smith),

¹⁾ Comp. Report April 1911, 72; October 1911, 49.

²⁾ The Technical Gazette of N. S. Wales, of 29/5/1911. From a reprint kindly sent to us.

³⁾ See Report April 1911, 73.

E. Rudderi, Maiden, *E. Baueriana*, Schauer (*E. subrotunda*, R. Br.; *E. polyanthemos*, Benth. non Schauer; *E. Fletcheri*, R. T. Baker with the var. *concolor*, Maiden and *E. cneorifolia*, D. C. (*E. stricta*, R. Br. non Sieb.; *E. hypericifolia*, Link; *E. myrtiformis*, Naudin [?]).

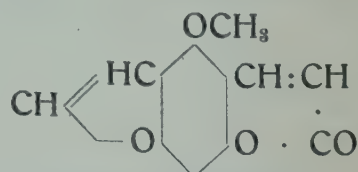
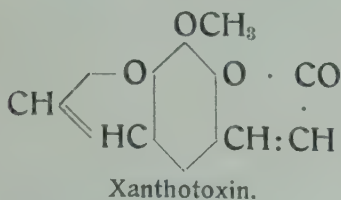
Oil of *Fagara Aubertia*, see **Oil of *Xanthoxylum Aubertia***, p. 13.

Oil of *Fagara xanthoxyloides*. In our last two Reports (April 1911, 7 October 1911, 49) we referred to xanthotoxin, an interesting body which has been found by Thoms in the root oil of *Fagara xanthoxyloides*. Even at that time, Thoms surmised xanthotoxin to be a coumarin-like compound, related to citroptene. His latest investigations¹⁾ have confirmed the correctness of this supposition. By extracting the shells with alcohol, Thoms obtained a solid substance (m. p. 128°) which was split up by repeated recrystallisation into two parts, xanthotoxin (m. p. 128 to 146°) and bergaptene (m. p. 190 to 191°), the latter a constituent of bergamot oil. The two bodies are isomeric, but bergaptene is a phloroglucinol derivative, whereas xanthotoxin is derived from pyrogallol.

Besides nitroxanthotoxin, which has already been described²⁾, Thoms prepared methylxanthotoxic acid (m. p. 114 to 117°) and methylxanthotoxin methylate (m. p. 44°). The isomeric methylbergaptene methylate melts at 52°. When melted with potash, pyrogallol carboxylic acid is formed, from which it is evident that xanthotoxin is a pyrogallol derivative to which the molecular structure reproduced below applies, assuming that no atom transposition takes place during the melting-process.

Experiments with sticklebacks showed that the narcotic power of xanthotoxin is considerably higher than that of bergaptene.

From a botanical point of view the occurrence of xanthotoxin and bergaptene in *Fagara xanthoxyloides*, and of bergaptene in the fruit of *Citrus Bergamia*, the parent-plant of bergamot oil, is interesting, for the two plants are closely related, belonging to sub-divisions of the same botanical family, namely: *Rutaceæ-Xanthoxyleæ* and *Rutaceæ-Aurantoidæ*.



Another body which has been isolated by Thoms and F. Thüme from the root-bark of *Fagara xanthoxyloides* by extracting with benzene

¹⁾ Berl. Berichte **44** (1911), 3325.

²⁾ Comp. Report October 1911, 50.

³⁾ Monatsh. f. Chem. **12** (1891), 379.

⁴⁾ Berl. Berichte **44** (1911), 3717.

is fagaramide, m. p. 119 to 120°, which has been identified by the authors as the *isobutylamide* of piperonylacrylic acid. They prepared the bodies synthetically from piperonylacrylic acid chloride and *isobutylamine* in ethereal solution. So far, the presence of this nitrogenous body in the oil of *Fagara xanthoxyloides* was unknown.

Fennel Oil. Our prophecy that only a slight reduction in the prices of fennel could be looked for in the course of the winter has come true. The farmers, almost without exception, have been able to obtain the prices for which they were standing out, and the oil-distillers in Galicia consequently remained firm in their turn. We have ourselves within the past few months distilled a quantity of fennel, so as not to leave in the lurch the numerous customers who appreciate our "extra" quality with high solidifying-point.

Garlic Oil. As is well known, garlic oil¹⁾ is one of the few oils which contain sulphur. According to Manindranath Banerjee²⁾ a ready method of estimating the sulphur-content is to triturate impure mercury containing lead in a mortar with garlic-juice, when lead sulphide, together with a minute proportion of mercuric sulphide, is formed. It is even possible by this means to free the mercury entirely from lead.

Geranium Oil. Since our last Report there has been a further considerable change for the worse in the position of the African geranium oil market. In so far as it was at all possible to procure any offers, the prices ranged between 55 and 60 francs, and these figures have actually been paid for various small lots which turned up here and there. Generally speaking, however, business in the article was extraordinarily quiet, inasmuch as consumers very strongly objected to pay such prices, and instead turned their attention in an increasing degree to substitutes, among which our pure geraniol takes the first place. Whether the high values of oil will induce growers who had abandoned their plantations in previous years on account of the low prices, again to take up geranium growing remains to be seen, but in any case it must be borne in mind that there is no prospect of a return to the old, brisk trading-conditions in geranium oil unless there is a considerable reduction in prices. The total exports of African geranium oil from Algeria in 1911 amounted to

28 500 kilos,	compared with
33 800	„ in 1910,
41 000	„ „ 1909,
46 000	„ „ 1908.

As was to be expected, therefore, the shipments again show a considerable falling-off last year.

¹⁾ Comp. Report October 1910, 68.

²⁾ Proceed. chem. Soc. 27 (1911), 234.

The position of Réunion geranium oil was uncertain at the time when our last Autumn Report went to press, for one reason because it was too early to say anything about the coming crop, and for another because sorts of contradictory rumours were current on the probable course of prices. Not until the end of December was it possible to state with some degree of certainty that the summer crop, which commences about this time, was likely to give a favourable result, although in some districts the growing crops had again been damaged by a cyclone. The prices sagged by a few francs, and might perhaps have returned to near their old level, if a well-known Grasse firm had not caused a sudden veering round in the tendency by speculative operations. The quotations thereupon again advanced by leaps and bounds, and it now remains to be seen whether the firm in question will succeed in carrying its speculative interference to a successful issue. Naturally, it is the consumers who pay, for they are compelled nilly-willy to concede the high prices as soon as their stocks are at an end. It is obvious that in these circumstances it is out of the question to pronounce an opinion on the future of the market. For the first time for a long period the exports of Réunion geranium oil show a decline, the shipments from St. Denis having been as follows: —

In the year 1911, 45 238 kilos

„ „ „ 1910, 64 156 „ .

Ginger Oil. A few large purchases of suitable distilling material at advantageous prices have enabled us steadily to replenish our stocks of ginger oil, and we have therefore been in a position to cope throughout with the brisk demand which has made itself felt in spite of the high prices. Unfortunately, the general scarcity of the article has undergone no alteration during the past few months, and the position must still be described as very firm.

Gingergrass Oil has been rather neglected, principally because those manufacturers who formerly were in the habit of buying the article regularly, have found in our exquisite palmarosa-oil substitute an adjunct which is at once cheaper and possessed of a finer odour. Under the pressure of lack of business the prices of the new season's gingergrass oil have receded to a level scarcely ever known in the past. In spite of this little interest is shown in the article, and wholesale transactions are at a standstill.

A sample of this oil distilled at Buitenzorg¹⁾ gave the following constants: d_{20}^4 0,928, $\alpha_D^{20} + 46^\circ 5'$. The yield was 0,1%.

Grape Fruit Leaf Oil see **Shaddock Leaf Oil**, p. 116.

¹⁾ Jaarb. dep. landb. in Ned.-Indië, Batavia 1910, 49.

Iva Oil. With the object of filling-in the somewhat incomplete chemical data available on the subject of iva oil, we have examined in some detail one of our most recent distillates. It had been prepared from the dry lowering herb, the yield being about 0,37% oil of a bluish-green colour and an intense, narcotic odour, which also reminded of valeric aldehyde, cineole and thujone. The constants were as follow: d_{150} 0,9330, n_{D200} 1,47607, acid v. 7,5, ester v. 18,7, ester v. after acet. 91,5, sol. in 0,7 vols. and more 70% alcohol, with elimination of paraffin. The presence of an aldehyde (valeraldehyde?), was revealed by the formation of a solid bisulphite-compound when the oil was shaken with bisulphite liquor, but the paucity of the quantity obtained precluded identification. Treatment of the oil with semicarbazide solution yielded a semicarbazone melting at 237,5°, the alcoholic solution of which was dextrorotatory, and which, when decomposed with dilute sulphuric acid, yielded camphor. As was to be expected from the optical behaviour of the semicarbazone, its ethereal solution was lævorotatory, hence there was no doubt of lævo-camphor being a hitherto unknown constituent of iva oil. In addition to this body, the oil appears to possess alcoholic constituents, partly esterified, partly in the free state, as is indicated by the saponification values of the original and the acetylated oil.

Juniper Berry Oil. In the course of last winter we have again worked up several wagon-loads of Italian berries, which on the present occasion constituted the most suitable material for our purpose. They were, it is true, dearer than other varieties, but thanks to the abundant yield we were able to leave our selling-prices unaltered. Hungarian juniper berry oil, as a result of the poor harvest, has been quoted from 0 to 15% higher this season than in 1910/1911.

Ladanum Oil. This as yet little-known oil¹⁾ is obtained from ladanum resin, which is an exudation of bush-like plants belonging to the genus *Cystus* indigenous to Asia Minor, Crete, Cyprus and a few other islands off the coast of Asia Minor. It has recently been investigated by J. Masson²⁾, who has found it to contain hydrocarbons, phenols, esters, ketones, and sesquiterpene-compounds. Masson now communicates the results of his investigations of the ketones. He treated a fraction boiling at 150 to 90° (15 mm.) with hydroxylamine hydrochloride, and obtained an oxime with b. p. 133° (16 mm.). From this oxime he regenerated the ketone, which, when purified from primarily produced semicarbazone (m. p. 207°), boiled at 200° (91° at 18 mm.) and was identified as acetophenone by oxidation into benzoic acid. So far this ketone had not been known to occur in volatile oils.

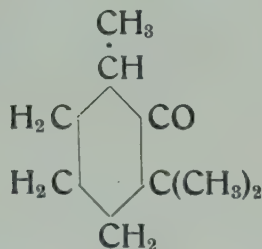
¹⁾ Gildemeister and Hoffmann, *The volatile oils*, p. 505.

²⁾ Compt. rend. 154 (1912), 517.

A fraction boiling between 70 and 78° (15 mm.) yielded an oxim. p. 106° (126 to 127° at 17 mm.) from which Masson obtained a ketone possessing the following properties: b. p. 178 to 179° (66 to 67° at 10 mm.) $d_{40} 0,922$, $\alpha \pm 0^\circ$, $n_{D_{23}} 1,4494$. This ketone did not react with bisulphite, it yielded a monobromide with m. p. 41° and a semicarbazone with m. p. 220 to 221°. With sodium and moist ether it was capable of being reduced to the corresponding secondary alcohol, which forms large crystals, m. p. 51° (b. p. 87° at 28 mm.). With cold 3% potassium permanganate solution the ketone was oxidised into geronic acid (b. p. 190 to 191° at 31 mm.; m. p. of the semicarbazone 164°), the latter, when oxidised with sodium hypobromite, giving rise to bromoform and α, α -dimethyladipic acid. This process of resolution has therefore shown the ketone $C_9H_{16}O$ to be trimethyl-1,5,5-hexanone-6, a body which has not been described up to the present.



Geronic acid.



Trimethyl-1,5,5-hexanone-6.

Laurel Oil. This article is suffering from decided over-production and we desire earnestly to impress upon the producers the need of reasonable moderation of output, for there is simply no outlet for such quantities as have recently been offered from Palestine and the Greek islands. The unwholesome position of the market has been correspondingly reflected in the downward course of prices.

Lavender Oil. We regret to report that our fears have been realized for in October and November the French dealers began to enter the market as buyers with such vigour that within a brief space of time the prices were driven up to 42 francs for oils of high quality. Fortunately, by the time we had already secured the greater part of our requirements (which always exceed the capacity of production of our Barrême works), and we may therefore leave to others whatever claims to distinction there may be in having driven up values without any particular reason. The principal stocks in producers' hands quickly found buyers at the prices indicated, and what supplies now remain in the first hand are either of important or of inferior quality. It is true, however, that the demand soon began to droop once more and that for the past three months practically no sales have been effected. In any case there are at present

signs whatever of an important change in the market, be it upwards or downwards, within the next few months, and it is too early of course to hazard an opinion concerning the coming crop. Generally speaking the rainy winter-weather has favoured the development of the plants.

F. Delphin has published two articles¹⁾ calling attention to two new lavender oil adulterants which have come under his notice. In the one case he concludes that in all probability the adulterant was cocoa-nut ether, although the acid which was separated out from the lavender oil in question, while possessing the same acid value as the acid from cocoa-nut ether, showed a decidedly higher iodine value and a somewhat lower m. p. These discrepancies, however, were to be explained by residual impurities from the lavender oil.

In the second case, Delphin found phthalic ester to have been the adulterant. The acid which was separated out from the saponified oil, after being purified and several times recrystallised, melted at $198,5^{\circ}$ with evolution of gas (phthalic acid from the anhydride melting in a similar manner at 198°) and gave the same reactions as phthalic acid.

By applying the method proposed in our Report of October 1910, p. 61, an adulteration with the esters in question (which belong to the esters of sparingly-volatile acids) would be detected, in the course of the determination of the difference between the saponification value and acid value II, by the increase in this difference. It would therefore be impossible to overlook it, and all that would remain to be done would be the identification of the acid in question.

In connection with the above we print a table containing the analytical values of a few samples of lavender oil submitted to us for our opinion. Sample No. 3 in this table is especially worthy of note, because here the abnormally low acid value II (with the corresponding excessive difference), together with the result of the test for terpinyl acetate and glyceryl esters appeared to point to sophistication, whereas in reality they were the result of a resinification. In such cases the sample in question should be rectified with steam. Renewed testing, together with the determination of the distillation-residue (which, in the case under review amounted to 8%), will then show whether the cause is adulteration or resinification.

As regards sample No. 5, with an ester-content of 51%, it is hardly necessary to point out that when 10 cc. seminormal potash liquor are used the required excess of alkali is too small, and that for that reason 15 cc. should be used. It follows that, to obviate erroneous conclusions in the test for terpinyl acetate, 30 or 15 cc. should then be employed under otherwise similar conditions.

¹⁾ Svensk Farmaceutisk tidskrift 1908, No. 22; 1912, No. 5. From a reprint kindly sent to us.

Samples No. 1 and 2 contained terpinyl acetate, while No. 4 was ulcerated with glyceryl ester, which was detected by shaking with 5% alcohol. 10 cc. of the filtrate obtained in accordance with the method described in our Report of April 1911, p. 150, used up 0,91 cc. seminor liquor. It was not possible, however, to identify the glyceryl acetate, sample at our disposal being too small.

L. Lamothe, to whose publications on lavender, its cultivation and its distillation, we have already repeatedly referred in these Reports¹⁾ calls attention in an interesting article²⁾ to the fact which up to the present has been but little noticed, namely the increasing cultivation and use of lavandin (*Lavandula fragrans* × *latifolia*, Chatenier). This species which is the result of a crossing of lavender and spike, is known in Southern France by several other names besides "lavandin", for instance "lavande bâtarde", "grosse lavande", "badasse", and others⁴⁾.

Lavender Oil	No. 1	2	3		4		5
			Original oil	Dist. with steam	Original oil	Shaken once with 5% alc.	15 cc. seminor liquor with potash
d ₁₅₀	0,9007	0,8946	0,9072	0,8932	0,8992	—	0,8913
α _D	—3° 55'	—2° 34'	—5° 14'	—5° 37'	—4° 32'	—	—8° 43'
Solub. in 70% alcohol	2,5 Vol.	2,5 Vol.	1,9 Vol.	2,2 Vol.	2,5 Vol.	—	4,5 Vol.
	a. m.	a. m.	a. m.	a. m.	a. m.		a. m.
Acid v.	0,3	0,5	0,8	—	0,5	—	0,3
Ester v. after 1 h. sap. with 10 cc. 1/2 n. liquor	78,4	83,3	100,5	102,5	90,0	87,0	145,7
Ester content (calc. for linalyl ac.)	27,4%	29,2%	35,2%	35,9%	31,5%	30,4%	51%
Ester v. after 2 h. sap. with 20 cc. 1/2 n. liquor	82,7	87,6	104,2	104,6	91,9	—	146,0
Ester v. after 1 h. sap. with 10 cc. 1/2 n. liquor + 25 cc. alc. . . .	69,7	77,0	99,0	100,6	91,1	—	144,1
Difference	13,0	10,6	5,2	4,0	0,8	—	1,9
Sap. v.	78,7	83,8	101,3	102,5	90,5	—	—
Acid v. II	75,7	83,7	96,7	100,6	90,6	—	—
Difference	3,0	0,1	4,6	1,9	—	—	—
Terpinyl acet. content about . .	5%	4%					
Esters of spar. vol. acids	not ascertainable		doubtful	not ascertainable	—	—	—
Glyceryl ester.	not ascertainable			not asc.	present	—	—

¹⁾ Report November 1908, 76; April 1909, 62; October 1911, 58.

²⁾ Parfumerie moderne 5 (1912), 9.

³⁾ For further details see the original article, and also the same author's pamphlet "Lavandin et Spic" (Report November 1908, 76). Also compare A. Birckenstock, "Action de l'hybridation des essences de lavande et aspic" (Report October 1906, 43).

⁴⁾ Lamothe also gives "grande lavande" as a synonym, and frequently uses this designation "lavandin" in his article. On the other hand in his brochure "Lavande et Spic", he differentiates between "grande lavande" (spike), and "grosse lavande" (lavandin).

Its flowers develop about a fortnight later in the season than those of the true lavender, which is ascribable to its hybrid character; spike, for example, flowers still later, in the beginning of September. Lavandin occurs principally in the region of the holm-oak, and even spreads beyond the boundaries of the latter, traversing in a broad belt the Departments of the Drôme, Vaucluse, Basses-Alpes, &c., where it covers the southern slopes of several mountains up to the top.

Like all hybrids, lavandin is an extraordinarily hardy plant, and in its prolific development constitutes an actual danger to the true lavender, which it robs of air and nourishment. The fact that this hybrid is gaining ground year by year gives cause for serious concern, the more so because pasturing sheep and goats shun it on account of its acrid odour and bitter taste, whereas in the true lavender these animals find an occasional welcome substitute for grass.

But in spite of this same bitter, herbaceous and camphor-like flavour, which places it far behind lavender as an odoriferous plant, very considerable quantities of lavandin are cut for distilling.

Lamothe estimates that the lavandin oil which is brought to market every year amounts to about 20 p.c. of the total output of lavender oil, or, in weight, to about 12 000 kilos. He regards this as most regrettable and utters an emphatic warning against the distillation of lavandin flowers, or although they yield a better return than true lavender, and with less trouble, their oil is decidedly inferior and may easily injure the present predominant position of French lavender oil. Lamothe gives a very interesting comparison of the respective outputs, which deserves to be quoted here. In the same time which is required to collect about 55 kilos true lavender flowers nearly 400 kilos of the freer-flowering lavandin can be gathered without trouble. And whereas for the production of one kilo lavender oil 145 kilos flowers are needed, from 77 to 80 kilos flowers suffice to produce one kilo of lavandin oil.

With regard to the properties of lavandin oil Lamothe states that the samples distilled by him had an average ester-content of 24%¹⁾. As in the case of true lavender oil a linalyl acetate content of 30% is considered low, this fact shows the inferiority of lavandin oil; but by estimating the ester-content it is always possible to guard against the use of an inferior product.

Lamothe not only warns his countrymen against the distillation of lavandin flowers, but also against their export, because here also the reputation of French lavender is likely to suffer as a result of the poor quality of these flowers. He has no doubt that such frauds are practised,

¹⁾ Compare Report October 1906, 44. A sample of "lavandin" oil examined by us gave the following constants: $d_{15} 0,8911$, $\alpha_D - 3^\circ 25'$, ester v. $51,5 = 18\%$ ester (calc. as linalyl acetate), sol. in 2 vols. a. m. 70% alcohol.

for many unscrupulous dealers are found who are in the habit of mixing flowers exhausted by distillation with the fresh lavender.

Lamothe advocates the total and permanent exclusion of the hybrid from all commercial uses, but at the same time he suggests that on account of its profusion in flowering and its hardy character it shall be given a place of honour as an ornamental plant.

E. Th. Brewis and J. C. Umney¹⁾ report on the changes which English lavender oil undergoes under certain circumstances during storing. The reason for the investigation was the fact that as a result of the high prices now ruling, supplies were being placed upon the English market which showed quite abnormal characters, indicating a percentage of esters so high as to lead to the idea that the oils were mixed with French oils. A more careful investigation, however, showed that the samples merely represented old oils which had become much resinified as the result of years of keeping. The oils were instantly distinguishable by their unpleasant, resinous, acetic odour. They also had an exceptionally high sp. gr., and in most cases the proportion of free acid and ester was uncommonly large. The sp. gr. varied according to the degree of resinification, the maximum being 0,9885, the acidity varied up to 3,22% (calc. as acetic acid) and the ester-content up to 22,7% (calc. as linalyl acetate). The corresponding values of normal oils were as follow: d_{15}^0 0,884 to 0,896, acidity 0, in one instance 0,12%, ester content 5,9 to 11%.

In view of the fact that the degree of resinification was independent of the age of the oils (a few oils even giving normal constants after more than 10 years' keeping), Brewes and Umney consider that the changes are connected with the percentage of moisture remaining in the oil, all essential oils containing a certain percentage of water dating from the time of their distillation. They are now engaged in studying the matter from this point of view, and they regard it as necessary that more attention should be given to the drying and storing of the oils than has been done at present.

The *Bulletin of the Imperial Institute* [9 (1911), p. 401] contains an article on lavender-growing in England²⁾. As we have only lately dealt at some length with the cultivation of lavender at Mitcham and in other districts of England, we will content ourselves with a mere reference to the article in question³⁾.

Lemongrass Oil. With the exception of a short period of pronounced dulness which occurred in December, the tendency of this important article has been firm throughout the last few months. The quotations fell from

¹⁾ *Perfum. and Essent. Oil Record* 3 (1912), 5.

²⁾ Quoted from *Journ. Board Agric. U. K.* 18 (1911), 566.

³⁾ Report October 1910, 75.

$4\frac{3}{4}$ d. per oz. in October to about $3\frac{1}{2}$ d. per oz. in December, but afterwards they returned to their present level of about $4\frac{1}{2}$ d. per oz. It is said that the stocks in India have shrunk within a small compass, and it is therefore probable that for some time to come a rising market will prevail. The only statistical figures available are as follows: —

Shipments of lemongrass oil from Cochin in the period
between 1st July and 31st January.

	1911/12	1910/11
To London	681 cases	676 cases
„ Hâvre	1343 „	1158 „
„ Marseilles . . .	3491 „	1538 „
„ Bremen	183 „	250 „
„ Hamburg . . .	893 „	765 „
„ New York . . .	972 „	235 „
	7563 cases	4622 cases

Although the above figures only give a very approximate clue to the consumption, for the size of the cases differs greatly, it is nevertheless remarkable that the shipments to Hâvre and Marseilles far exceed those to the other ports. We believe this fact to warrant the inference that the present principal consumers of lemongrass oil are France and Switzerland. It will also be seen that the exports in 1911/12 have considerably increased as compared with those of 1910/11.

The Imperial Institute in London¹⁾ reports on several samples of lemongrass oil of different origin. The oils came from Ceylon, India, Uganda, Bermuda, and Montserrat. As, with one exception, we have already referred to the Ceylon oils (Report April 1911, 79), a bare mention may here suffice. It only needs to be added that the samples of this oil described by the Imperial Institute, in common with the distillates of *Cymbopogon citratus* previously mentioned, belong to the class of sparingly-soluble lemongrass oils. The oils from the other localities belong to the same group; an oil from Cochin alone being more readily soluble. This oil the Imperial Institute classes among the “soluble” lemongrass oils, although even with 90% alcohol it did not afford a solution which remained clear when diluted. It is true that, differing in this respect from the other oils, it gave a clear solution with 2 vols. 70% alcohol, but even this solution turns turbid when more of the solvent is added. The other constants of the oils are set forth in the subjoined table p. 90.

The distillation of lemongrass oil in Uganda was undertaken at first by Government, and in the year 1909/10 the export amounted to 16 603 ozs.

¹⁾ Bull. Imp. Inst. 9 (1911), 334.

of a value of £ 72. The preparation of the oil has now been taken up by a business-house. The parent plant, according to a determination made at the London Botanical Gardens, is *Cymbopogon citratus*, which accounts for the imperfect solubility of the oil.

We have previously described a lemongrass oil from Uganda (Report April 1909, 65).

Origin	d_{15}^0	α_D	Citral content (Bisulphite method)
Ceylon	0,9058	— 0° 6'	76 ⁰ / ₀
India, Tyrna . . .	0,9021	— 0° 20'	72,5 ⁰ / ₀
„ Cochin . . .	0,9053	— 0° 39'	84,5 ⁰ / ₀
„ Mariani . . .	0,9140	— 0° 5'	73 ⁰ / ₀
Uganda	0,870 to 0,894	+ 0° 10' to — 0° 24'	64,5 to 75 ⁰ / ₀
Bermuda	0,8689	— 0° 21'	40 ⁰ / ₀
Montserrat . . .	—	—	over 74 ⁰ / ₀

Brooks¹⁾ describes the oil of an as yet unknown *Andropogon*-species which is evidently closely allied to lemongrass oil. The constants of the oil were as follow: d_{30}^{30} 0,8777, $\alpha \pm 0$, n_{D30} 1,4868, and it contained about 72⁰/₀ citral (m. p. of the semicarbazone 155 to 160°) and 12⁰/₀ geraniol. The latter was isolated by means of the calcium chloride compound.

Limette Oil. We have recently received from our well-tried, reliable source of supply fresh shipments of the finest hand-pressed oil, so that up to the present we have been able to satisfy the requirements of the numerous customers who have been attracted in the course of years by our exquisite quality. Unfortunately the shipments have been less plentiful of late, and we have therefore already been compelled to increase our prices. The demand for our terpeneless limette oil has also been very animated.

Oil of Limnophila. According to Brooks²⁾ the leaves of a species of *Limnophila* (N. O. Scrophulariaceæ), which occurs in the Philippines, yield about 0,2⁰/₀ of an oil with a rosemary-like odour and a density of 0,850.

Linaloe Oil. The market in Mexican linaloe oil has been greatly neglected throughout the winter months, but in spite of this there has been no decline in prices worth mentioning. The main reason for the great neglect of the article must no doubt be sought in the competition of the exquisite Cayenne linaloe oil, which was obtainable at remarkably cheap rates and of which the quality is far superior to that of the Mexican

¹⁾ Philippine Journ. of Sc. 6, A. (1911), 351.

²⁾ Philippine Journ. of Sc. 6, A. (1911), 345.

oil. The difference in price between the two oils being only small, those who, like ourselves, consume large quantities of the oil in the manufacture of linalol and linalyl acetate, prefer the Cayenne oil to the other. A few parcels of Mexican oil consigned to Hamburg were moreover of such inferior quality as hardly to deserve the name of linaloe oil. The shippers in Cayenne continued to complain of the low prices, but in the end there was no other course open to them but to sell their oil at the price of the day, unless they wished to have it thrown on their hands. But at the beginning of February a serious rise took place in bergamot oil, and suddenly such a demand set in for linalyl acetate and other substitutes that the linaloe oil market recovered within a few days. In the end 19 *M* was asked for Mexican oil, while Cayenne oil rose quickly from 19 francs cif. Hâvre to 30 francs. Thus far the prices of both oils have been maintained at this level, and the demand remains exceedingly keen; their further course will mainly depend upon the position of the bergamot oil market. We understand that at a selling price of 19 to 20 francs the manufacture of Cayenne linaloe oil is far from paying, especially because of late, owing to the drying-up of the water-courses, the conveyance of the wood from the primeval forest to the distilling-place has become difficult. In how far the revolution which is now again spreading in Mexico will affect the linaloe oil market is a problem for the future. According to a report by the British Vice-Consul in Cayenne, the exports of linaloe oil from French Guiana have been as follows: —

In the year 1908,	7 470 kilos,	value 186 750 Francs,
" " " 1909,	12 497 " "	312 400 " ,
" " " 1910,	22 066 " "	551 650 " .

These figures clearly show the enormous increase of the linaloe oil industry in Cayenne.

The distillation of a large quantity of Cayenne linaloe wood afforded us an occasion for investigating more closely the distillation-waters as well as the first runnings of the oil. The cohobation-water still contains considerable proportions of oil, and especially of linalool, and in addition to these there occur two aldehydes which have already been observed on several occasions in the distillation-water or in the first runnings, or both, of essential oils. These aldehydes are furfural and, possibly, *iso*-valeraldehyde. We isolated the furfural by treating the oil obtained from the cohobation-water with bisulphite liquor. The aldehyde boiled between 159 and 161° and had d_{150} 1,160; with β -naphthylamine it gave the well-known colour-reaction; the phenylhydrazone melted between 96 and 98° and the semicarbazone at 196°. In comparison with furfural the first runnings only contain very small proportions of *iso*-valeraldehyde. Judging from the irritating, cough-compelling odour and from the b. p. (90 to 95°)

it is most probably present. The thiosemicarbazone had no uniform m. p., as it was impossible to remove the small quantities of furfural which were present.

The cohobation-oil, when freed from its aldehydes, contained, in addition to methylheptenol (Report October 1911, 60), cineole, which we identified from its iodol-compound, m. p. 110 to 111° and its constants; and dipentene, of which the dihydrochloride melted between 47 and 48° and the tetrabromide between 124 and 125°. The cineole-content of the first runnings varied between 30 to 40%.

In addition to cineole and dipentene, the first runnings appears to contain an aliphatic terpene. It was impossible to isolate this body by fractionation; by acting upon it with glacial acetic and sulphuric acids we obtained a yield of about 10% of an ester of which the alcohol, after saponification, melted between 210 and 215°, and had $d_{15} 0,915$. This alcohol resinified very readily; its odour reminded both of linalool and of terpineol. As the fraction with m. p. 168 to 170°, which had been used for hydration, contained no sabinene, camphene, fenchene, or pinene, the surmise that the alcohol has been generated from an aliphatic terpene is probably not quite unfounded.

The observations recorded above are in agreement with the detection in Mexican linaloe oil of an olefinic terpene, announced by us a few years ago (Report April 1909, 67). It is highly probable that this body is identical with myrcene.

In our Report of October 1910 (pp. 26 and 79) we mentioned that a so-called linaloe oil had recently been prepared in Formosa. We have since learnt from the *Chemiker-Zeitung*¹⁾ that a licence for preparing this oil has been granted to the firm of Mitsui Bussan Kaisha, who hope to distil 300 kilos of the oil before March 31st of this year. No further news has been received regarding the botanical origin of the product.

We believe the oil to be probably identical with apopin oil (described in our Reports of October 1903, 10 and April 1904, 10) or with a fraction of that oil.

On the preparation of dihydrolinalool from methylheptenone of various origin, see p. 177.

Oil of *Magnolia glauca*. The leaves of this North American shrub (*Magnolia glauca*, L.; N. O. Magnoliaceæ) contain, according to a communication by F. Rabak²⁾ 0,05% of a pale-yellow essential oil: $d_{25} 0,9240$, $[\alpha]_D + 3,96^\circ$, $n_{D25} 1,4992$, acid v. 1,8, ester v. 13, ester v. after acet. 28, gives a cloudy solution in 3½ vols. 90% alcohol, insoluble in 80% alcohol.

¹⁾ Chem. Ztg. 36 (1912), 89.

²⁾ Midland Drugg. and pharm. Review 45 (1911), 486.

Melaleuca Oils. In our last April Report (p. 81) we referred to the oils of *Melaleuca trichostachya* and *bracteata*, which Baker and Smith had discussed in a paper read before the Royal Society of N. S. Wales. Since then the authors have published more precise details on these distillates¹⁾, from which we abstract the following: Oil of *Melaleuca trichostachya*, Lindl.²⁾ is obtained from the dry leaves, the yield being from 1,25 to 2,58%, and the constants as follow: d_{150} 0,9144 to 0,9153, $\alpha_D + 2,3$ to $3,1^\circ$, n_{D20} 1,4636 to 1,4655, sap. v. 2,1 to 2,8, ester v. after acet. 13,9, soluble in 1,3 vols 70% alcohol. In addition to about 80% cineole (determined by the resorcinol method), the oil probably contains pinene. As regards esters, the authors proved the occurrence of terpinyl acetate; they identified the terpineol from the reaction with hydriodic acid (formation of dipentene dihydriodide, m. p. 77°). The oil further contains traces of phenols and of low-boiling aldehydes, as well as a sesquiterpene(?), sp. gr. 0,934; n_D 1,4985.

Oil of *Melaleuca bracteata*, F. v. M. This oil, which is prepared from the leaves and branches (yield 0,643 to 0,964%) possesses the following constants: d_{180} 1,032 to d_{190} 1,0358, $\alpha_D - 1,4$ to $- 3,1$, n_{D20} 1,5325 to 1,535, acid v. 0,7 to 1,26, sap. v. 5,3 to 20,8. Ester v. of the saponified oil after acet. 24,57, sol. in 0,7 to 0,8 vols. 70% alcohol. It contains 0,36% eugenol (m. p. of the benzoyl compound 68 to 69°), 0,33% free cinnamic acid as well as cinnamic acid in combination (m. p. 133°), traces of cinnamic aldehyde, a little *l*-phellandrene (m. p. of the nitrite 120°), cinnamyl-cinnamate(?), and 70% methyl eugenol (estimated by Zeisel's method), identified from its bromide, m. p. 77 to 78° , and from oxidation into veratric acid, m. p. 178 to 179° .

Mr. Baker was kind enough to send us, together with a reprint of his paper, a sample of oil of *Melaleuca bracteata*. It was of a yellowish colour and possessed an agreeable odour, reminding somewhat of champaca oil. d_{150} 1,0422; $\alpha_D - 1^\circ 10'$; n_{D20} 1,53428; acid v. 0,4; ester v. 20,8; ester v. after acet. 31,0; sol. in 1,5 vols. a. m. 70% alcohol.

The leaves of *Melaleuca stypheloides*, Sm. also afforded an essential oil, but in such exceptionally small proportions that it was impossible to determine its constants.

Oil of Micromeria japonica, Miq. According to Y. Muragama³⁾ the air-dried herb of this labiate contains 0,7% of a yellow oil, with a characteristic odour of peppermint. Fractional distillation of the oil yielded *l*-menthone, which was identified from its boiling point, combustion and the preparation of the oxime. It is possible that the oil also contains menthol.

¹⁾ Journ. and Proceed. Royal Soc. of N. S. Wales 44 (1911), 592. From a copy kindly send to us.

²⁾ According to Baker and Smith, *Melaleuca trichostachya* and *linariifolia* are not synonymus, as stated in the *Index Kewensis*, but represent distinct species.

³⁾ Journ. pharm. Soc. of Japan 1911, 783. Quoted from Zeitschr. d. allg. österr. Apoth. Ver. 50 (1912), 48.

Mustard Oil. Contrary to expectation, the demand for the natural distilled oil has not declined to the extent which we anticipated in our last Report, and we have therefore only recently commenced the distillation of another large parcel of mustard seed. It is a fact, however, that there is less demand for natural mustard oil than formerly, and only Russia still remains a regular customer for quantities of some importance. Generally speaking users have turned to the artificial mustard oil, and in this they are quite justified.

It has often been asserted that black mustard does not contain enough myrosin to split up the whole of the glucoside sinigrin which also occurs in it, and in order to increase the yield it has even been recommended to add white mustard during the process of fermentation. Experiments in this direction which have been made by H. J. Greenish and Dorothy J. Bartlett¹⁾ have shown the assumption with regard to the insufficiency of myrosin to be incorrect. Not only does the seed contain enough myrosin to split up the sinigrin which is also present in it, but the proportion of the enzyme is occasionally large enough to decompose thirteen times the quantity of sinigrin in the seed.

As was to be expected, the addition of white mustard during fermentation does not improve the oil-yield in the slightest degree.

According to Greenish and Miss Bartlett the addition of sodium fluoride to mustard seed during fermentation (as recommended by Brioux)²⁾, is very effective, 0.4% of the fluoride being sufficient. Fluoride of sodium does not injuriously affect the action of myrosin, but it kills the micro-organisms which destroy the allyl sulphocyanate.

Interesting also is the observation made by Greenish and Miss Bartlett that black mustard of the 1905 crop when examined in 1911 showed a normal myrosin-content; from which it appears that myrosin is not injured by prolonged storage of the raw material.

Myrtle Oil. To the myrtle oils of special origin which have been described in our previous Reports³⁾ must be added an Algerian oil which has recently been examined by us. Its properties agree with those of the Corsican oil: d_{150} 0.8871, $\alpha_D + 25^\circ 52'$, n_{D200} 1.46466, acid v. 1.1, ester v. 20.6, ester v. after acet. 39.2, sol. in 0.5 vol. a. m. 90% alcohol.

Oil of *Nepeta Nepetella*. *Nepeta Nepetella*, L. is the name of a Labiate which grows fairly plentifully in the neighbourhood of Saint-Auban (Maritime Alps)⁴⁾. The plant possesses a peculiar odour of peppermint. The oil (yield 0.0598%), distilled after the close of the flowering season,

¹⁾ Pharmaceutical Journ. 88 (1912), 203.

²⁾ Annales de Chimie analytique 17 (1912), 6.

³⁾ Report April 1909, 71; April 1910, 78; October 1911, 61.

⁴⁾ Berichte von Roure-Bertrand Fils, October 1911, 41.

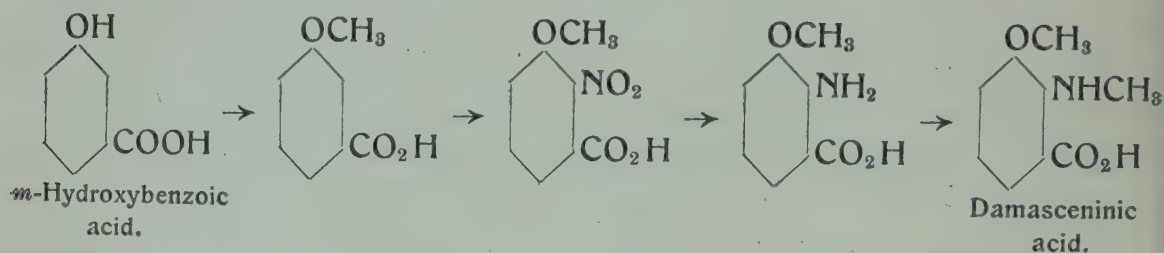
was heavier than water and constituted a yellow, somewhat viscous liquid possessing the following properties: $d_{20} 1,03984$, $d_{32} 1,02536$, $\alpha_D + 15^\circ 12'$, α_D of the acetylated oil $+ 17^\circ 20'$, acid v. 45,5, ester v. 245,7, ester v. after acetylation 314,5. It was soluble in 2 vols. 70% alcohol; when more alcohol was added the mixture turned cloudy. A solid body with an odour of menthol was isolated from the oil; the saponification-liquor, after being acidulated, yielded an oil possessing an odour of caprylic and of valeric acid at the same time. Only a portion of the oil was absorbed with bisulphite.

Neroli Oil. It is many years since the winter-rainfall on the Mediterranean coast of France has been so heavy as that of last season, and the trees have therefore been flourishing. As a result of the wet weather, however, some of them have already flowered prematurely during the early months of the year, and these will show a proportionate deficiency during the flowering-time proper in the month of May, but taking it all-in-all the prospects are highly favourable, and unless night-frosts should supervene a good medium-crop may be expected with certainty. There can be no doubt, however, that the yield will not approach that of last season, which was well above the average. At the moment the buds look very healthy and it may be expected that, barring unforeseen circumstances, the gathering will this season commence about 15th April, that is to say about a fortnight sooner than usual. It is thought that the flower-prices will not rule high: at present the talk is of 65 to 70 centimes, for both of neroli oil and of orange flower water there is some stock left over from the year 1911. Naturally, however, the Société coopérative de production des propriétaires d'orangers des Alpes-Maritimes will energetically defend the interests of its members, and will distil all the flowers which it is unable to place with the manufacturers at remunerative prices. For the present it is of course impossible to say much concerning the probable course of the neroli oil prices, which have remained unchanged, with slight fluctuations, throughout the past winter. In the year 1911 the Société coopérative harvested 1800000 kilos flowers, or about 500000 kilos more than usual. Of this output, the Society was compelled to distil about 550000 kilos, because there was no market for this surplus, but the Society was able to dispose of the bulk of the oil thus obtained at prices ranging from 475 to 500 francs per kilo. Just at present there is more pressure to sell, and from several quarters there have been forecasts of a price of about 400 francs for oil of the new crop. The flower-production of the Société coopérative is estimated at rather more than two-thirds of the total flower-crop in the Department of the Maritime Alps; hence it would seem that the total yield of the orange flower crop of the year 1911 has been about 2600000 kilos.

The sale of our artificial neroli oil "Schimmel & Co." last year attained a magnitude previously unthought-of, and as there is now a large number

of regular users of this splendid substitute who formerly absolutely refused to have anything to do with it, it may be confidently anticipated that this article will continue to grow in favour, no matter whether the prices of true neroli oil rise or fall. In the matter of uniformity of quality our artificial neroli oil is decidedly superior to the natural oil.

Nigella Oil. Damasceninic acid, a derivative of damascenine, which is a constituent of nigella oil, has been obtained synthetically by A. J. Ewins¹⁾ from *m*-hydroxybenzoic acid by a series of reactions represented below. As Keller²⁾ has shown that it is possible to convert damasceninic acid into damascenine, it follows that the last-named body may be prepared synthetically by Ewins' method.



Nutmeg oil. There has been no lack of nutmegs rich in oil and suitable for distilling purposes. We have again worked up several large parcels and have thus been in a position to replenish our stocks, which had been greatly depleted by brisk sales during the months of November and December, and particularly by large orders from the United States.

Nutmeg-tree Bark Oil. At Buitenzorg³⁾ the sap. v. of this oil (which has been mentioned by us on a previous occasion)⁴⁾ has been determined at 14; ester v. after acet. 37.5. The oil contained no aldehydes.

Oil of *Ocimum sanctum*. Some time ago we stated⁵⁾ that, according to Bacon, the oil of *Ocimum sanctum*, L. contains considerable quantities methylchavicol. Brooks⁶⁾, who has recently investigated the product, also found methylchavicol to be its principal constituent (50 to 60%), besides which he found cineole and linalool present. The cineole afforded the characteristic hydrobromic acid compound.

Origanum Oil. An oil of *Origanum hirtum*, Link., which shows a marked similarity to an oil from the same parent plant which has been examined by us⁷⁾, is described by S. S. Pickles⁸⁾. The raw material, which

¹⁾ Proceed. chem. Soc. 27 (1911), 277.

²⁾ Comp. Report April 1908, 73.

³⁾ Jaarb. dep. landb. in Ned.-Indië, Batavia 1910, 49.

⁴⁾ Report April 1911, 83.

⁵⁾ Report April 1911, 83.

⁶⁾ Philippine Journ. of Sc. 6, A. (1911), 345.

⁷⁾ Report October 1911, 63.

⁸⁾ Proceed. chem. Soc. 27 (1911), 284. See also Bull. Imp. Inst. 9 (1911), 388.

was obtained from Trieste, yielded 3,3% oil: d_{150} 0,9440, $\alpha_D + 0^\circ 24'$, soluble in 2,8 vols. 70% alcohol. It contained from 66 to 67% thymol.

Another sample of origanum herb, which had been received from Trieste by the Imperial Institute in London¹⁾, and was found to be derived from *Origanum Onites*, L., yielded upon distillation an oil of precisely similar properties to those of a distillate from the same plant described by us a year ago (Report April 1911, 85): d_{150} 0,9483, $\alpha_D - 1^\circ 15'$, sol. in 2,75 parts a. m. 70% alcohol. The phenol-content, consisting almost entirely of carvacrol, was 68%.

Orris Oil. Business in both varieties of orris oil has been somewhat sluggish lately, and only began to show signs of revival when it became known that the stocks of Florentine orris root were unusually small and when prices, consequently, began to tighten. The following passage is translated literally from the report of our local correspondents:—

“Since our last report on Florentine orris root the prices have continually risen, a result of numerous orders which heavily reduced the existing stocks. According to our previous communications the supply was as follows:—

Stock in hand at end of August 1911	about	90 tons
add 1911 crop	”	600 ”
	Total: about	690 tons,

against which must be set off the total deliveries from the beginning of September 1911 until the end of February 1912	”	570 ”

Hence the available stock on 29th February 1912 amounted to about 120 tons.

The present market price is $\mathcal{M}$ 90.— per 100 kilos cif. Hamburg for sorts; of pickings scarcely anything is left. According to our last report the average annual exports for the nine years from September 1902/August 1903 to September 1910/August 1911 amounted to about 690 tons, as compared with an average crop in the eight years 1903 to 1910 of about 650 tons. The crop of 1911, amounting to about 600 tons only (the raw root yielded fully 20% less of trimmed root this year than last, apparently owing to the great drought), reduces the average yield of the nine crop-years 1903 to 1911 to about 644 tons. On the other hand the deliveries during the last half-year, from the beginning of September 1911 until the end of February 1912, have been very considerable, amounting to about 570 tons, and it may be taken as fairly certain that when the new crop begins to arrive on the market at the end of August there will be no old supplies whatsoever left to start the new season with. As regards the next crop, the estimates so far agree that it will not only not exceed the last in quantity but will even fall considerably below it.”

In view of the conditions presented above, we are compelled to accept the probability of a considerable advance in the price of orris oil within

¹⁾ Bull. Imp. Inst. 9 (1911), 388.

the next few months, and we therefore advise those of our customers who desire to take advantage of our present selling-prices, which are based upon our previous purchases of raw material, to lay in their supplies in good time.

Parsley Oil from seed. Raw material suitable for distillation has been very hard to find as, owing to the severe drought, but little seed had been gathered last year. When suddenly an animated demand for parsley oil arose from France the prices advanced considerably, but owing to the small stocks available only a small part of this demand could be satisfied.

Oil of *Parthenium argentatum*. *Parthenium argentatum*, Gray (N. O. Compositæ), a native of Mexico, is an interesting plant, for, as we learn from a paper by P. Alexander¹), it yields (calculation based upon dry substance), from about 8 to 10% of rubber-material (the Guayule-rubber of commerce), whereas the rubber-content of *Hevea brasiliensis*, the parent-plant of the Pará rubber, can only amount to a few ‰ of its total weight. The comparatively high rubber-content of *Parthenium argentatum* is explained by the fact that, as is the case in all rubber-yielding plants, the cells containing the milky juice occur exclusively within the tissues of the bark. In a dwarf-shrub, such as *Parthenium argentatum*, this tissue constitutes a considerable proportion of the entire plant, whereas in a giant tree such as *Hevea* it only amounts to a fraction of the whole weight.

In addition to rubber the plant, calculation based upon dry material, contains about 0,5% essential oil.

For the purpose of preparing this oil material grown in Mexico was used which had probably been collected and dried quite shortly before shipping. It yielded about 0,015% of a greenish-yellow, faintly lævo-rotatory oil²), (d_{150} 0,8861), consisting entirely of hydrocarbons. Under fractional distillation at 17 mm. 30% passed over between 50 and 60°; 20,3% between 60 and 80°, and 24,8% between 120 and 160°; the residue amounting to 5,5%. The oil contained *l*- α -pinene (m. p. of the nitroso-chloride 100 to 102°; m. p. of the nitrolbenzylamine 122°) and a constituent with a pepper-like odour, the latter being the carrier of the odoriferous substance of the oil: b. p. 130 to 140° (17 mm.), d_{150} 0,9349, $[\alpha]_{D180}$ — 21°24', n_{D180} 1,496. Alexander surmises this body to be a sesquiterpene, but he was unable to identify it with any of the known sesquiterpenes.

Another oil, distilled from material which had been in warehouse for some considerable time, proved to be rich in oxygen and, when distilled, left a residue of about 50% resin.

¹) Berl. Berichte 44 (1911), 2320.

²) The scanty oil-yield is due to the fact that no suitable distilling-plant for large-scale work was available.

At the conclusion of his paper Alexander pronounces oil of *Parthenium argentatum* to possess a marked similarity to oil of German chamomile. We are unable to judge in how far the odour of the two oils is similar, but they certainly differ altogether in their chemical constitution.

Patchouli Oil. This important article, too, gives rise to little comment upon the present occasion. The serious advance in price of patchouli leaves has so far been without material effect upon the price of patchouli oil, although the supplies are beginning to be light. It would seem, however, as if in all quarters ample supplies had been laid in of this article, the value of which notoriously improves with keeping; at any rate the demand moves within very moderate limits. It is also evident that the consumers have at last adopted our view that the patchouli oil distilled in Europe by careful and scientific methods is superior in aroma to that imported from Java and the Straits Settlements, for the parcels of oil which have been imported during the last few months have been very difficult to place, notwithstanding the reductions in price conceded by the owners.

We have referred in previous Reports to de Jong's investigations¹⁾ into the oil-content of patchouli leaves in various stages of development, and it will therefore be sufficient here to state the fact that de Jong has recently published another paper on the subject²⁾.

Pennyroyal Oil. There has been no change recently in the neglected condition of the market for this oil; the demand is extremely small, and in the producing countries but little interest is now shown in the article, because the output of the last few crops has only been saleable at a very moderate profit, if not at an actual loss.

American pennyroyal oil, from *Hedeoma pulegoides*, Pers., as prescribed by the U. S. Pharmacopœia, has remained scarce throughout the period under review, and the supplies will scarcely hold out until the new crop comes in. Quite recently, according to a communication received from our New York branch, an oil described as "false Pennyroyal Oil", which reminds strongly of rosemary oil, has repeatedly been offered from the Southern States. We hope to be in a position, later on, to give some information concerning the botanical origin of this oil.

The *Pharmaceutical Journal* [87 (1911), 652, 700] contains an article on the etymology of the term "Penny" in the word "Pennyroyal". It is thought that this term may be a corruption of the word "pulliol", the Old English designation of the pennyroyal mint being "Pulliol Royal".

¹⁾ Comp. Report November 1909, 95; October 1909, 92.

²⁾ Recueil trav. chim. des P.-B. 30 (1911), 211. From a reprint kindly sent to us.

Pepper Oil. We have been afforded an opportunity of securing several large parcels of raw material at advantageous prices, and have thus been able once more to replenish our stocks for some considerable time ahead. We have proportionately reduced the price, but we are further prepared to quote special rates to any customers who are prepared to consider the purchase of quantities of some importance.

Peppermint Oil, American. Our New York expert is of opinion that the firmness of this oil during the whole of the past year is due in the first instance to the fact that even before the crop was ripe a few of the dealers had made large contracts with the principal farmers at comparatively high prices. These contracts kept up the quotations and thus helped to tide over a somewhat dull period, which set in when it was found that, after all, the distilling had yielded a larger output than had originally been expected. The total production of oil in 1911 is now estimated at 240000 lbs. In the late autumn and in the winter a brisk demand made itself felt, resulting in a large turnover at rising prices, which, however, did not deter consumers in the United States. The stocks now in the hands of the producers, amounting to only about 30000 lbs. together with the quantity still left in second hand, will hardly be sufficient to cover the requirements until the arrival of the new crop. For this reason the view prevails in America that an increase in prices may be looked for within the next few months as soon as any considerable demand arises, or if buyers should fail to observe the necessary caution. As is well-known, the trade in American peppermint oil in Europe is dominated by our well-tried brand of rectified oil "F S & Co." This trade has been in a thoroughly satisfactory condition throughout the whole of last year. We were able to supply our principal customers in good time on advantageous terms, and the turnover considerably exceeded that of previous years.

It is still too soon to express an opinion on the effect of the long and severe winter upon the peppermint-fields, but if the spring-weather should be favourable and no late frosts should hurt the roots, the tightening of prices which is to be expected will doubtless induce the growers to extend the cultivation. It will therefore be advisable not to lay in supplies beyond July or August at the present prices.

Peppermint Oil, English. The position is unchanged, and the expected advance has not taken place. In fact, consumers are becoming more and more convinced that this article is much too dear at the present prices, and for this reason they are turning in an increasing measure towards our American brand "F S & Co." As a result of the painstaking method of selection practised by our New York branch the quality of the last-named brand has within the past few years been brought to a degree of excellence which is able to satisfy the most exacting requirements with

respect to pure peppermint-aroma. So far no reports are available concerning the condition of the peppermint-plantations in England.

Peppermint Oil, French. The cultivated species of *Mentha*, and in particular *Mentha piperita*, have been examined botanically by A. and E. G. Camus¹⁾. *Mentha piperita* does not constitute a separate species, but is a hybrid of *Mentha viridis* and *Mentha aquatica*. It may be regarded as a sterile plant, as it fruits rarely, and even then the fruit is mostly badly-developed, hence the plant must be propagated by sub-dividing the rhizomes. Like all *Mentha*-species, *Mentha piperita* is extraordinarily variable. To add to the confusion, different varieties are cultivated in various plantations under the common denomination of "peppermint". Several varieties also

	Ordinary Peppermint		Red Peppermint	
d_{150}	0,9191	0,9184	0,9170	0,9136
" D	— 10° 54'	— 8° 2'	— 16° 38'	— 13° 44'
Solubility in 80% alcohol . . .	1 vol. afterwards clouding	—	1 vol. afterwards clouding	—
Acid v.	0,8	0,8	1,0	1,2
Ester v.	40,5	31,7	18,9	17,5
Menthyl acetate	14,3%	11,2%	6,7%	6,2%
Ester v. after acet.	160,8	169,1	180,2	185,6
Total Menthol	50,9%	53,9%	58,0%	60,0%
Free Menthol	39,6%	45,1%	52,8%	55,1%
Proportion of Menthone	7,3%	—	16,8%	—

occur of the original species. *Mentha piperita* embraces two groups; group I including the subspecies *piperita*, Briq. with numerous varieties, while group II includes the sub-species *citrata*, Briq., which under the name of "citronelle" is much grown in France because of its pleasant aroma, but which does not appear to be used commercially. In its internal structure *Mentha piperita* exhibits certain features midway between those of *Mentha viridis* and *Mentha aquatica*. How variable are the *Mentha*-species is shown by *Mentha viridis*, L. and *Mentha aquatica*, L.; for the authors describe no fewer than six varieties of the former, and as many as eight of the latter, besides indicating many others.

As a complement to their botanical review the authors give the analytical peculiarities of the essential oils from the ordinary and from the

¹⁾ Berichte von Roure-Bertrand Fils, October 1911, 3.

so-called red peppermint. These are set forth in the table below. The red variety has only been cultivated in the South of France comparatively recently. It yields rather more oil (about 0,33%) than does the ordinary peppermint (about 0,25%), but its oil is not of so fine a quality as that of the last-named. Red peppermint will grow on soil where the ordinary variety can barely live. It may even be grown for five years in succession on the same land, while in the case of genuine peppermint it is necessary to interrupt the cultivation every third year¹).

Peppermint Oil, Japanese. We will abstain from correcting the statements relative to the probable yield of the crop which appeared in our last Report, because the news of the production in the various districts which has been received since then is again of such a contradictory character that the later figures would be of no greater value than those which have already been published. The only particular in which the reports agree is the admission that the result of the Hokkaido crop was considerably over-estimated last autumn. A large part of the crop is said to have been destroyed by floods, while another part has suffered to such an extent from the so-called "rust-worm" that it became necessary to cut the peppermint before it reached maturity, as a result of which there has been a serious loss of oil. This much, in any case, is certain, that all attempts to induce the Japanese to moderate their demands for oil and menthol have been fruitless, and remain so at the going to press of the present Report. Within the past few days, as a matter of fact, there has been a further decided increase in the quotations. Seeing that the demand in Europe is remarkably brisk and that several speculators will be compelled shortly to cover their bear-sales, we believe that considerably higher prices will rule within the next few months. A fairly long time still separates us from the new crop, and as it is our experience that the consumption, especially of menthol, has greatly increased of late, we regard it as highly probable that a decided scarcity will make itself felt in the course of the summer. Very much will depend, of course, upon the American peppermint-crop, of which the probable result, however, cannot be estimated for the present.

In the course of fractional distillation of a first runnings of Japanese peppermint oil we obtained a fraction giving b. p. 175 to 181°; $d_{15} 0,8436$; $\alpha_D - 84^\circ 27'$; $n_{D20} 1,46773$. It consisted chiefly of *l*-limonene, which was identified from its tetrabromide, m. p. 103,5 to 104,5°. As the fraction reacted faintly with sodium, we heated a small quantity with this metal. After distilling off the oil which had not been affected by the reaction and removing the unattacked sodium, we diluted the sodium-compound with

¹) On French peppermint oil also comp. Reports April 1905, 62; October 1906, 58; October 1907, 74; April 1909, 76; April 1911, 90.

water and distilled the resulting isolated oxygenous constituents with steam. A strong menthone odour still adhered to these constituents, which were treated with phthalic anhydride in order to isolate the alcoholic parts, the result being an acid phthalate which was readily soluble in the usual solvents. The crude product melted between 62 and 63°, the m. p. rising to between 64 and 65° after recrystallisation from benzene. Finally, when recrystallised from ether and chloroform, it gave m. p. 64,5 to 65,5°. The alcohol which was regenerated from the phthalate constituted an oil with an odour strongly reminding of secondary octyl alcohol: b. p. 57 to 58° (3¹/₂ mm.), d_{150} 0,8296, $\alpha_D - 0^\circ 10'$, n_{D200} 1,42652. When oxidised with bichromate of potassium and sulphuric acid the alcohol gave rise to a ketone of which the odour somewhat reminded of methylhexyl ketone. But it was evidently not this ketone, as was proved by the fact that it gave no reaction with neutralised sodium bisulphite solution. Moreover, the semicarbazone did not give the characteristic m. p. of methylhexyl ketone semicarbazone.

For the purpose of closer investigation we subjected a fraction possessing 'similar properties to that referred above to direct treatment with phthalic anhydride. The characters of this fraction were as follow: d_{150} 0,8521, $\alpha_D - 52^\circ 26'$, n_{D200} 1,45991. The product which was recovered from the phthalate gave identical constants with the alcohol which was prepared from the previous fraction: b. p. 56° (3¹/₂ mm.), d_{150} 0,8279, $\alpha_D + 6^\circ 17'$, n_{D200} 1,42775. These constants underwent scarcely any change as the result of distillation under ordinary pressure: b. p. 178,5 to 179,5°, d_{150} 0,8276, $\alpha_D + 6^\circ 26'$, n_{D200} 1,42755. Oxidation with sodium bichromate and sulphuric acid yielded a ketone which did not react with bisulphite. The product which was regenerated from the semicarbazone (m. p. 117°) possessed the following properties: b. p. 170°, d_{150} 0,8255, $\alpha_D + 0^\circ 22'$, n_{D200} 1,41556. Apart from its low optical activity, which appears to be due to traces of impurity, the ketone possesses the constants of an ethyl-*n*-amyl ketone which was isolated by us some years ago from French lavender oil, and which were as follow: b. p. 169,5 to 170°, d_{150} 0,8254, $\alpha_D + 0^\circ$, n_{D200} 1,41536. A mixture of the semicarbazones of the two ketones suffered no depression of m. p. The above facts may be held to afford proof that the alcohol formed by us represents *d*-ethyl-*n*-amylcarbinol, $C_2H_5CH(OH)C_6H_{11}$.

We oxidised the alcohol with the calculated quantity sodium bichromate and sulphuric acid, and obtained capronic acid, proof being afforded by the b. p., the odour and analysis of the silver salt.

0,1543 g. substance: 0,0757 g. Ag.

Found	Calc. for $C_6H_{11}AgO_2$
Ag 49,06%	48,42%

With phenylisocyanate no phenylurethane was formed; α -naphthyliso-

cyanate, on the other hand, gave rise to an α -naphthylurethane, m. p. 81 to 82° (from dil. methylalcohol).

We are at present engaged in preparing the alcohol synthetically, and in identifying it by preparing a few of the esters.

A new colour-reaction has been recommended for distinguishing Japanese peppermint oil from peppermint oils of other origin¹⁾. We will content ourselves with placing the matter on record here because we only employ tests of this kind in exceptional cases, seeing that they lack all scientific foundation, and fail, moreover, in the case of mixtures. The author heats 1 cc. of the oil with 0,5 gram of a mixture of equal parts paraformaldehyde and citric acid over a water bath. With Japanese peppermint oil there is no decoloration, whereas with American, English, Italian (and as our tests show with Saxon oils also), a purple colour develops. This new test has the advantage of being quicker than the familiar colour reaction with concentrated acetic acid.

On the presence of *d*-neomenthol in Japanese peppermint oil see p. 180.

Peppermint Oil, Russian. A few years ago²⁾ we reported on a peppermint oil which came from the Province of Tambov, in Central Russia. Recently, according to a statement by Maisit³⁾ the cultivation of peppermint has also been taken up in the Caucasus, where the climate is more favourable, and where the plant is said to flourish so well that South Russian peppermint oil has been for some time a commercial article in the Russian home market. In the District [of Sotshi, situated on the Black Sea, the black variety of English peppermint (*Mentha piperita*, Mitcham var. *nigra*), is chiefly cultivated. It is grown at an altitude of about 1500 feet and is distilled in newly-erected, modern distilling plant. According to the growers' statements the dried herb of the flowering plant yields from 1,6 to 1,7% of crude oil.

Oil from	d_{20}^o	α_D	Acid v.	Ester Menthol	Free Menthol	Total Menthol
First year's plants	0,912	— 17° 42'	0,57	6,57%	42,44%	49,17%
Second year's plants	0,913	— 17° 57'	0,57	8,74%	41,33%	50,07%

Both oils were sparingly soluble in 70% alcohol, and when placed in a freezing mixture menthol began to separate out only after prolonged standing.

¹⁾ Perfum. and Essent. Oil Record 2 (1911), 275.

²⁾ Report April 1907, 82.

³⁾ Arch. der Pharm. 249 (1911), 637.

As will be seen from the table above, there are no remarkable differences in the constants of the oils. Maisit noticed that both oils, when distilled under ordinary pressure, left a remarkably high residue, about 18%. He ascribes this to the fact that both samples were crude distillates, but in our view the reason is more likely to have been that in the course of fractionation without reduction of pressure a partial decomposition of the oils took place.

Oil of *Persea pubescens* (Pursh.), Sarg¹). This laurel is a native of the central parts of North America and is commonly known as "swamp red bay" or simply as "swamp bay". According to Rabak²), the leaves contain 0,2% of an oil possessing the following properties: $d_{25^{\circ}} 0,9272$, $\alpha_D + 22,4^{\circ}$, $n_{D25^{\circ}} 1,4695$, acid v. 2,8, ester v. 14,5, ester v. after acet. 64, sol. in $\frac{1}{3}$ vol. 80% alcohol, the solution turning turbid when 5 vols. or more is added. Rabak detected in the oil only one free acid, viz., butyric acid; but it contained both butyric and valeric acids in the esterified state as well as slight proportions of cœnanthic acid. Other constituents observed were: 21% *d*-camphor (m. p. of the semicarbazone 237 to 239° ; m. p. of the oxime 117 to 118°), 19,8% cineole (m. p. of the hydrobromide 55 to 57°) and possibly small quantities of borneol and formaldehyde.

Petitgrain Oil, Paraguay. The pessimistic prognostications of our correspondents have unfortunately proved to be well-founded, and during the last few months it has been more difficult to procure fresh supplies than has perhaps been the case at any previous time. The revolution in Paraguay has adversely affected the industry, and to this obstacle has been added an inundation which has crippled the few distilling plants that had escaped the revolutionary disturbances. As a result the prices have risen, but it seems as if they had hardly yet reached their highest point, inasmuch as for the present there appears to be no prospect whatever of any improvement in the conditions. According to a report by the German Consulate of Asuncion³), the exports of petitgrain oil in the year 1910 amounted to 28 056 kilos, which shows a falling-off of nearly 2000 kilos compared with 1909⁴).

Oil of *Peucedanum Ostruthium*. F. Lange⁵) has recently investigated the oil of *Peucedanum Ostruthium*, Koch, the properties of which are as yet little known. The oil had been distilled from the dry roots of two year old plants grown in the Tyrol, the yield being 1% and the characters as follow: $d_{20^{\circ}} 0,8627$, $\alpha_{D20^{\circ}} + 59,30^{\circ}$, acid v. 0,8, sap. v. 17,9, ester v. after acet. 28,34. In addition to free palmitic acid the oil contained

1) *P. carolinensis*, Nees of the Index Kewensis.

2) U. S. Dep. of Agriculture, Bureau of Plant Industry, Bull. No. 235, p. 29.

3) Nachrichten f. Handel u. Industrie, 4 December 1911.

4) Comp. Report October 1910, 106.

5) Arbeiten aus dem pharm. Inst. der Univers. Berlin 8 (1911), 98.

the following bodies in the esterified form: *isobutyric acid*, *isovaleric acid*, *isopropylidene acetic acid* (β , β -dimethylacrylic acid), formic acid and acetic acid. It is uncertain whether *isopropylidene acetic acid* was present in the original oil or whether it was only generated during the distilling process.

The oil contained 95% terpenes, among which the following were identified: dipentene (m. p. of the dihydrochloride 50°), *d*-limonene (m. p. of the nitrolbenzylamine 92 to 93°), α -pinene (m. p. of the nitrolbenzylamine 122 to 123°) *d*-phellandrene (m. p. of the nitrite 103 to 104°). The oil also contained an alcohol $C_{10}H_{20}O$ (?), of which the phenylurethane melted at 145 to 146° . Finally, Lange detected the presence in the oil of a sesquiterpene, which yielded a dihydrochloride melting at 157 to 157.5° .

Angelicaldehyde, which is mentioned by Wagner as a constituent of the oil, was not found in it by Lange.

Pimento Oil. It has been necessary to raise the price in the course of the winter, because the arrivals of pimento of a quality suitable for distilling have been very scanty and raw material has commanded higher rates. For the present there does not seem to be any prospect of a reduction, as the demand is much in excess of the production.

Pine-needle Oils. The principal interest continues to be centred upon Siberian pine-needle oil, because that variety occupies a specially favoured place among the oils which are adapted for all kinds of technical purposes and at the same time possesses the advantage of cheapness. The aroma of this oil is so pleasant and powerful that it has also secured for the article an opening in numerous manufactures which formerly relied exclusively upon the more costly varieties of pine-needle oils. Pine-needle oil from *Abies pectinata*, and oil from the cones (*Ol. templinum*), were in plentiful supply; on the other hand the distillation of oil from *Pinus Pumilio* is being restricted in some of the producing districts, because this manufacture no longer pays at the present depressed selling-prices, and because it is becoming a more and more difficult and costly matter to procure the raw material for distilling. For the present it is impossible to say in how far this fact will influence the course of prices in the near future.

We seize this opportunity to point out once more that for many years past oils have been placed upon the market from various districts, which, although of quite excellent quality, possess a rather lower specific gravity and a higher optical rotation than are ordinarily considered admissible in oil of *Pinus pumilio*. We have already called attention to this matter in a previous Report (October 1906, 62) and we will now only add the supplementary statement that it is absolutely necessary to recognise the existence of these deviations from the normal, as other oils are at times unprocurable.

The same observation applies to the slight differences in odour which are observable in pumilio oil, and which occasionally lead to complaints by customers that a certain parcel of oil supplied to them does not possess a sufficiently fine aroma. In the case of an article such as pumilio oil, which is being distilled all through the year, small deviations in scent are quite unavoidable, for it is obvious that differences in the degree of maturity of the material worked up will make themselves felt in the odour of the oil also, which therefore varies according to the season when the oil was distilled. The difference is not important, but it is of course noticeable by the expert. It is quite impossible to guarantee to supply pumilio oil of which the scent will always be the same.

Oil of *Pluchea foetida*. The green herb of *Pluchea foetida*, D. C. (*P. camphorata*, D. C. of the *Index Kewensis*), N. O. Compositæ, yields according to F. Rabak¹⁾ 0,025% of a pale golden-yellow essential oil: $d_{20} 0,9329$, $\alpha_D - 5,4^\circ$ (in a 50 mm. tube), $n_{D20} 1,4845$, acid v. 4,1, ester v. 44, sap. v. after acet. 104. It is soluble in its own volume of 80% alcohol, the solution turning cloudy upon the addition of 5 vols. a. m. Cineole (m. p. of the iodol-compound 113°) was found to be a constituent of the oil.

Oil of *Ramona stachyoides*. *Ramona stachyoides* (Benth.), Briquet, (*Audibertia stachyoides*, Benth.; *Salvia mellifera*, Greene) is a shrub-like labiate which occurs in Southern California and is there known as "black sage". The green flowering plant, distilled by Rabak²⁾, yielded 0,75% of a colourless oil with a camphoraceous odour, possessing the following properties: $d_{20} 0,9144$, $\alpha_D + 30,2^\circ$, $n_{D20} 1,4682$, acid v. 2, ester v. 2,5, ester v. after acet. 27,1, sol. in 1,5 vols. 70% alcohol, the solution turning turbid when more than 3,5 vols. is added. At -15° 11,3% *d*-camphor (m. p. 174 to 175° ; m. p. of the semicarbazone 232 to 233°) is separated out from the oil. Rabak's sample contained small quantities of formic acid in the free state, while acetic acid and possibly traces of formic acid were present in combination. The oil also contains about 22,5% cineole (m. p. of the iodol compound 111 to 112°) and possibly pinene, thujone and borneol. Its total camphor-content is about 40%.

Rasama Oil. Rasama oil³⁾, a volatile oil, has been found at Buitenzorg⁴⁾ to possess the following constants: $d_{20} 0,924$, $\alpha_D - 51^\circ 24'$. The principal part of the oil appears to consist of sesquiterpenes: b. p. 250 to 258° .

Rose Oil, Bulgarian. The Bulgarian rose oil market has during recent months been under the influence of a pronounced lack of business, and although certain wealthy firms have tried with great pertinacity to

¹⁾ Midland Drugg. and pharm. Review 45 (1911), 485.

²⁾ U. S. Dep. of Agriculture, Bureau of Plant Industry, Circular No. 235, p. 14.

³⁾ The original reference contains no particulars of the parent-plant.

⁴⁾ Jaarb. dep. landb. in Ned.-Indië, Batavia 1910, 50.

maintain the price at about 2000 francs per kilo (the figure which it had reached in September 1911), they were nevertheless compelled, as time went on, to show a more tractable spirit in order not to be left with their stocks on hand. As no orders of any magnitude came forward, prices finally receded to about 1700 francs per kilo. At that level, however, they have remained steady, because in the meantime news has been received from the growing districts, announcing that the plantations have been seriously damaged by the severe winter, and that the prospects of the new crop have again become unfavourable. In any case, however, it is still too soon to express a reliable opinion on the probable development of the flowers. The weather during the months of April and May will be the chief determining factor in this respect.

In Gildemeister and Hoffmann's book *The Volatile Oils* (p. 429) the maximum limit of value of the optical rotation of rose oil is stated to be $\alpha_D - 4^\circ$. Afterwards¹⁾ we reduced this limit to -3° . Later, in our Report of October 1910 (p. 111), we called attention to the fact that Parry had examined six samples of rose oils alleged to be pure, of which the optical rotation ranged from -4° to -5° , whereas in our own experience we had only once encountered a sample with $\alpha_D - 4^\circ 20'$. More recently, a few instances have again occurred in which Bulgarian rose oils, when examined in our laboratory, have shown an optical rotation exceeding -4° , their constants in other respects being normal. Quite lately another such oil came under our notice. Its constants were: $d_{300} 0,8608$, $\alpha_D - 4^\circ 32'$, $n_{D250} 1,46565$, sol. p. $+19^\circ$, acid v. 1,5, ester v. 9,5, total geraniol 68,3%. When the oil was washed out with water its specific gravity remained unaltered, but the co-efficient of refraction had risen to 1,46704, a value which had never before come under our notice in rose oil of good quality (compare Report April 1910, 93).

Our suspicion that the sample under examination represented an adulterated article was confirmed by the striking discovery that the stearoptene which had separated out from the oil was semi-liquid at ordinary temperature and rotated strongly, whereas the stearoptene of rose oil of normal condition is at most feebly active, and is solid at room-temperature. It was therefore evident that a liquid material possessing strong optical rotatory power had been added to the oil. Upon further examination of the oily constituents, which in each case had again been freed from solid paraffin by freezing, we obtained, among other fractions, one which possessed the following physical characteristics: b. p. 95 to 96° (4 mm.), 255 to 260° (756 mm.), $d_{150} 0,9203$, $\alpha_D - 63^\circ 55'$, $n_{D200} 1,49975$.

After being saturated with hydrochloric acid gas in an absolute ethereal solution the oil afforded no solid hydrochloride even when left to stand

¹⁾ Report October 1904, 81.

for several days. Combustion showed the fraction to consist of a hydrocarbon $C_{15}H_{24}$, only slightly contaminated by oxygenous constituents.

0,4062 g. substance: 1,2836 g. CO_2 , 0,4194 g. H_2O .

	Found	Calc. for
C	86,18 %	88,23 %
H	11,48 %	11,77 %

For purposes of further purification the hydrocarbon was treated with metallic sodium and resolved into separate fractions. By this method we finally isolated an oil possessing the following constants: b. p. $95,5^\circ$ (4 mm.), 258 to 261° (756 mm.), d_{15° 0,9206, $\alpha_D - 81^\circ 56'$, n_{D20° 1,50049.

The fraction was treated for obtaining nitrosate and nitrosochloride, but without positive result. The strong lævorotation of all these fractions appeared to indicate that they might consist of gurjun balsam oil. Now it is well-known that some time ago Deussen and Philipp¹⁾, by oxidising gurjun balsam oil with permanganate in acetone solution, obtained a reaction-product which, it appears, may serve as a criterion for the detection of the addition of gurjun balsam oil to other oils, a view which is borne out by our present experience. The oxidation-product, b. p. 175 to 178° (12 mm.), is according to Deussen a ketone, and is sharply characterised by a semicarbazone melting at 234° and rather sparingly soluble in alcohol. The fractions of our sample with the strongest rotatory power had already been used up for other reactions, and for the purpose of oxidation only the two following fractions, amounting in all to about 14 g., were left:

- (1) B. p. 255 to 260° , $\alpha_D - 50^\circ 32'$,
- (2) B. p. 260 to 262° , $\alpha_D - 48^\circ 53'$.

The oil was dissolved in about 200 g. acetone, diluted with 35 g. water, and to the clear solution were gradually added 15 g. solid powdered permanganate. The unattacked oil, which boiled at 104 to 105° (5 mm.) was removed by fractionation and the distillation-residue treated with semicarbazide. The reaction-product was left standing overnight, when, after the addition of water, it was deposited as an oily precipitate, solidifying in part after prolonged cooling in ice under stirring with alcohol. The semicarbazone, repeatedly recrystallised from hot alcohol, had m. p. 234° , and, with a semicarbazone of the same m. p. and constants, prepared from gurjun balsam oil for purposes of comparison, suffered no depression of m. p. These two bodies were therefore identical.

From the result of the above examination it is to be concluded that the strongly lævorotatory oil which had been added to the stearoptene of the rose oil consisted principally of gurjun balsam oil, which had been improperly added to the rose oil for purposes of adulteration. Possibly

¹⁾ Liebigs Annalen 369 (1909), 56; 374 (1910), 105. Report April 1910, 146.

an adulterant previously observed by Parry¹⁾, which possessed a high rotatory power may also have been gurjun balsam oil, or a mixture of that oil with some other substance, for Parry states that this addition had also raised the alcohol-content of the oils. It will therefore be advisable to keep this adulteration in view for the future. In the isolation of the rose-oil stearoptene, gurjun balsam oil is precipitated together with the stearoptene, and it may therefore be desirable to extend the examination of rose oils in this direction and to submit the stearoptenes to closer examination, at any rate in all cases in which the rotation of the oil in question exceeds $-2^{\circ}30'$.

We may quote particulars of two other samples of rose oils which have been examined in our laboratory in the course of the past few months. The first represented a rose oil which had been offered to us for pur-

	No. 1		No. 2	
	Original oil	Extracted with water	Original oil	Extracted with water
d_{300}	0,8755	0,8793	0,8639	0,8667
α_D	$-20^{\circ}36'$	$-21^{\circ}50'$	$-1^{\circ}21'$	$-1^{\circ}23'$
n_{D25}	1,48042	—	1,45901	1,46664
Sol. p.	$+10,7^{\circ}$	—	$+18,0^{\circ}$	$+17,0^{\circ}$
Acid v.	1,0	—	1,8	1,7
Ester v.	7,6	—	19,1	20,0
Ester v. after acet.	119,9	—	249,7	240,3
Total geraniol.	36,2%	—	84,5%	80,6%
Quantity of added alcohol ²⁾ . .	6,5%	—	6%	—

chase, and which every analyst, even upon cursory examination, would have rejected as highly adulterated on account of the great abnormality of its constants. Apart from the alcohol which we discovered to be present in it (see the table below), it is possible that this oil was also adulterated with gurjun balsam oil, but the sample at our disposal was unfortunately too small to permit of its examination for this adulterant.

The second sample submitted to us for our opinion had already been examined in another quarter and, singularly enough, had been pronounced to be unobjectionable, notwithstanding that a carefully executed control-test made by us easily showed it to be also adulterated. (For the method of testing compare Reports November 1908, 107, and April 1910, 93.) This sample contained in the first place about 6% spirit, calculated for 90% alcohol. In the next place, the specific gravity and coefficient of refraction of the

¹⁾ Chemist and Druggist 77 (1910), 261; Report October 1910, 111.
²⁾ The alcohol was isolated as such.

de-alcoholised oil were outside the limits of value of rose oil, and furthermore the total-geraniol content (even after removal of the alcohol, which would have been converted by acetylation into acetic ester, and as such would likewise have raised the saponification value of the acetylated oil) was considerably too high, from which it was to be inferred that either palmarosa oil or geraniol had been added to the sample in addition to the other adulterants.

Rose Oil, German. The exceptionally cold weather of last winter, during which the thermometer on occasions fell to -22°C , has been well-supported by our rose-plantations, and unless, as was the case last year, there should be night-frosts in May or June, the prospects of our Miltitz rose-crop for the present year may be described as very bright indeed. At present it remains doubtful, however, whether, in spite of the extension of our plantations last autumn, we shall collect sufficient raw material to enable us again to take up the distillation of oil. The manufacture of our new speciality "Red Rose Schimmel & Co." (see p. 147), which has the natural flower as its basis, and of which the peculiar properties place it in the front-rank of all rose-products, requires such large quantities of newly-gathered roses, to make us fear that the whole of our output will be taken up by this branch of our works.

Rosemary Oil. The position of the rosemary oil industry in the South of France is by no means bright, for the fact must be plainly admitted that the monopoly of quality, which was formerly in the hands of the French, now appears to be a thing of the past. Although, speaking generally, the distillation of such oils in Spain is not conducted with particular care, that country has recently been placing upon the market ever-growing quantities of oil which is in no respect distinguishable from the French distillate. The prices of the Spanish oil are considerably lower than those of the French, and as the distillers in Southern France have been complaining for years that there was no profit in the article, it would appear as if the days of the Southern French rosemary oil industry were numbered. In sympathy with the slight demand for Dalmatian rose oil the producers of that article have somewhat lowered their pretensions of late. Just recently there are reports that the coming crop will be a failure, but in view of the lessened demand we doubt, for the present, whether these reports will greatly affect the prices.

Samphire Oil. The distribution of the essential oil in the leaves, stems and flower-parts of samphire (*Crithmum maritimum*, L., N. O. Umbelliferæ) has been described by L. Francesconi and E. Sernagiotto¹).

Sandalwood Oil, East Indian. Our anticipations of the probable course of the sandalwood prices have been amply confirmed: throughout the winter the tendency was very firm, and for the important sales which

¹) Rendiconti della R. Accademia dei Lincei (5), 20, II. (1911), 249.

nave been effected the buyers have been compelled to pay higher rate. A glance at the comparative tables on pages 114 and 115 of this Report showing the prices realized at the two series of auctions in 1911 and 1912 will be sufficient to convince the reader that the oil-quotations are fully warranted, and if account be taken of the probability that all the cheap lots held over from former years have been worked up in the meantime, and that the demand is growing from year to year, it will be hard to discover any logical reasons for a decline in prices.

How irksome the sandalwood oil business must have become for a few competing firms, especially abroad, is most clearly seen from the fact that from time to time these firms attempt to sell off some part of their output far below the current price, merely in order to avoid having the oil (which generally bears evidence of having been distilled in the most primitive way) left on their hands. Offers of this kind recur periodically, but they remain without the slightest effect upon the market because, of course, the standard of price is set only by a perfect distillate containing 94% santalol, such as is supplied by us. We have already fully described the size and importance of our sandalwood oil department in a previous Report. All through the winter our plant has been working day and night, yet we have been unable to accumulate stock, which surely proves in the most striking manner possible that the superiority of our distillate is appropriately acknowledged by the consumers. According to the reports at present available the future of the article can only be described as very firm, and we think that we may with a clear conscience advise our friends to choose the present moment for covering their requirements.

There is, we think, little doubt that as soon as the wood from last autumn's auctions is brought to the stills a further advance in the price of oil will be unavoidable. The complaints by capsule-manufacturers of depression of the prices of their product by extreme competition still persist, and we strongly recommend our numerous customers in this branch of industry to remember that the services of our research-laboratory are gratuitously at their disposal whenever they are faced with competition at prices which seem to indicate that the article thus offered is adulterated. We are quite prepared to allow our friends to make what use they please of our expert-opinion, if need be even in a court of law. Possibly this repeated reminder may in a few instances help to put a check upon the malpractices.

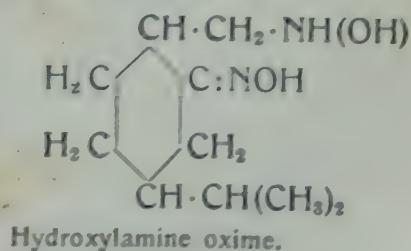
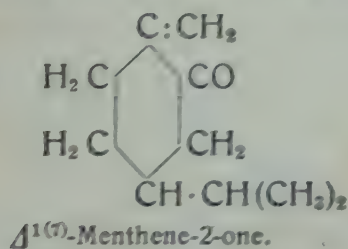
We have recently had occasion to examine an East Indian sandalwood oil taken from the capsules which had been sent to us for our opinion, and found it to possess the following characters: d_{150} 0.9688, α_D — $19^\circ 30'$, ester v. after acet. 152.3, equal to 67.5% santalol, insoluble in 70% alcohol. In this case it was obvious that there had been adulteration with cedarwood oil, inasmuch as, with a normal rotation, the sp. gr. was much too low, and the solubility so imperfect that the oil was altogether insoluble

in 70% alcohol. From the low santalol content it may be inferred that the adulterant constituted about one-third of the oil.

From a note in *The Chemist and Druggist* [79 (1911), 612] we also gather that in the adulteration of oil sold in the form of capsules the residues of santalol manufacture are being used as well as West Indian sandalwood oil. The principal market for capsules thus adulterated is said to be Australia, where the capsules are sold at prices barely covering the cost of the oil. Several samples recently examined had the following characters: $d_{15} 0,962$ to $0,966$, $n_D + 8^\circ$ to -4° , insoluble in 10 vols. 70% alcohol.

Sandalwood Oil, West Indian. In this article also there has been no excessive accumulation of stocks during the past few months. It is true that heavy consignments of wood have reached us regularly, but the demand has kept a fairly equal pace with the production, while large orders from the United States kept the deliveries at a steady level. At present the prospects remain unchanged, but there have lately been many rumours of difficulties in transport in Venezuela, and it is possible that ultimately, as a result of such difficulties, the wood may become dearer.

Santolina Oil. This oil, which was described in our last Report (p. 108), has already been examined in the same year by L. Francesconi and P. Scaraffia¹⁾. The authors, by using the reagents which they had already employed on previous occasions, *viz.*, osmic acid, ferric chloride solution and dilute alcoholic "Soudan-III" solution (see p. 31), discovered the essential oil to be principally located in the epidermic tissues. The yield varied from 0,198 to 1,15% according to the stage of development of the plant, being highest shortly before the flowering. The constitution of the oil likewise varies according to the period of maturity of the plant. The average constitution of the oil was C 81,68%, H 11,28%, O 7,04%, and its average constants as follow: $d_{15} 0,8732$, $[\alpha]_{D20} - 11,74^\circ$. The first fractions contained a terpene (b. p. 165 to 170°) and probably a phenol ether. With hydroxylamine hydrochloride the oil yielded an oxime and a hydroxylamine oxime. The corresponding ketone, which Francesconi and Scaraffia call santolinone, they regard as $\Delta^{1(7)}$ -menthene-2-one. The hydroxylamine oxime melts at 190° with previous softening at 180 to 185°.



¹⁾ Atti R. Accad. dei Lincei, Roma (5), 20 (1911), II. 255, 318, 383. Kindly sent to us by the authors. Quoted from Chem. Zentralbl. 1912, I. 344, 345.

Sandalwood auctions 1911.

Description	Tirthahalli		Sagar		Shimoga		Tarikere		Chikmagalur		Hassan		Bangalore		Seringapatam		Hunsur		Fraserpett		Total	
	Nov. 13		Nov. 16		Nov. 20		Nov. 23		Nov. 27		Nov. 30		Dec. 4		Dec. 13		Dec. 16		Dec. 18		Total	
	Tons	Cwts.	Tons	Cwts.	Tons	Cwts.	Tons	Cwts.	Tons	Cwts.	Tons	Cwts.	Tons	Cwts.	Tons	Cwts.	Tons	Cwts.	Tons	Cwts.	Tons	Cwts.
1st Class Billets .	—	—	—	—	—	—	—	4	—	3 ^{1/4}	—	3 ^{1/8}	—	—	—	—	—	—	—	—	—	10 ^{3/8}
2nd " .	—	7	—	15	1	13 ^{1/4}	4	6	1	15	8	5	2	16 ^{3/4}	9	5	4	10	20	—	66	6
3rd " .	8	15	—	—	17	13 ^{1/4}	7	8	1	18	1	1	—	12 ^{1/2}	9	15	5	10	5	—	58	1
Ghotla	2	7	—	—	2	11 ^{3/4}	8	6	1	5	1	13 ^{1/8}	—	4 ^{3/4}	3	10	3	10	—	—	23	12 ^{1/8}
Ghatbadala	5	10	12	12	69	3 ^{1/4}	40	9	51	10	22	2	13	—	9	10	45	—	20	—	288	16 ^{1/4}
Bagaradad	—	6	3	—	12	1 ^{1/2}	7	5	2	17	6	10	—	12 ^{5/8}	3	5	11	15	15	—	62	11 ^{1/8}
1st Class Roots .	9	6	8	3	30	5	10	—	* 2	19	12	3	15	2 ^{1/4}	6	10	15	5	10	—	141	18 ^{1/4}
2nd " .	9	13	4	8 ^{3/4}	13	—	10	5	* 3	10	6	1 ^{1/2}	7	6 ^{1/8}	9	5	22	10	10	—	95	18 ^{3/8}
3rd " .	7	6	3	10 ^{1/8}	13	8	9	—	—	18	3	16	3	6 ^{7/8}	6	15	11	10	7	10	67	—
1st " Jugpokal	57	15	21	5 ^{3/8}	78	15	58	10	46	10	20	10	27	1	29	10	86	5	25	—	451	1 ^{3/8}
2nd " .	16	7	8	9	17	—	14	—	6	—	6	15	6	13 ^{7/8}	13	10	36	—	10	—	134	14 ^{7/8}
Ain Bagar	6	12	5	—	7	15	10	5	3	4	4	1 ^{1/2}	4	4 ^{3/4}	4	10	13	15	5	—	64	7 ^{1/4}
Cheria	3	13	—	15 ^{1/4}	3	2 ^{1/2}	1	5	—	5	—	11 ^{1/2}	—	6 ^{3/4}	—	15	3	5	—	—	13	19
Ain Chilta	10	7	8	19 ^{1/4}	18	—	28	10	7	8	4	10	3	6 ^{1/4}	9	10	30	—	2	10	123	1 ^{1/2}
Hatri Chilta	—	13	—	1	1	5	—	5	—	4 ^{1/2}	—	13	—	—	—	10	—	3	—	—	3	14 ^{1/2}
Milwa Chilta	29	3	16	3 ^{1/4}	67	10	28	—	37	5	16	—	8	15 ^{1/4}	30	5	44	10	27	10	305	1 ^{1/2}
Basola Bukni	17	8	7	10 ^{1/4}	18	10	11	15	10	2	6	12	8	13 ^{1/4}	13	10	16	—	15	—	125	1 ^{1/2}
Saw Dust	—	9	—	7 ^{3/4}	—	17 ^{1/2}	—	7	—	4	—	6	—	—	—	5	—	15 ^{1/2}	—	—	3	11 ^{3/4}
Total	185	17	100	10	385	17 ^{3/4}	250	—	200	10 ^{3/4}	121	12 ^{3/4}	102	3	160	—	350	3 ^{1/2}	172	10	2029	4 ^{3/4}

* Last season's wood

Comparative prices obtained at the sandalwood auctions of 1910 and 1911.

Prices realized	Tirthahalli		Sagar		Shimoga		Tarikere		Chikmagalur		Hassan		Bangalore		Seringapatam		Hunsur		Fraserpet	
	17 12 1910	13 11 1911	14 12 1910	16 11 1911	8 12 1910	20 11 1911	5 12 1910	23 11 1911	1 12 1910	27 11 1911	28 11 1910	30 11 1911	24 11 1910	4 12 1911	21 11 1910	13 12 1911	17 11 1910	16 12 1911	15 11 1910	18 12 1911
2nd Class Billets	cif. d. w. p. cwt.	—	cif. d. w. p. cwt.	—	cif. d. w. p. cwt.	53/6	cif. d. w. p. cwt.	53/6	cif. d. w. p. cwt.	—	cif. d. w. p. cwt.	53/6	cif. d. w. p. cwt.	54/6	cif. d. w. p. cwt.	54/6	cif. d. w. p. cwt.	54/6	cif. d. w. p. cwt.	53/6
3rd "	53/6	53/6	—	—	55/6	54/—	54/—	54/—	—	—	—	—	—	—	54/6	—	54/6	—	53/6	—
Ghotla	52/	52/	—	—	—	—	52/9	—	—	—	—	—	—	—	52/6	—	51/6	—	53/6	—
Ghatbadala	52/6	47/3	44/—	46/9	45/3	48/3	46/6	46/—	45/9	50/—	45/—	50/6	44/6	50/9	43/3	51/9	45/9	52/3	44/6	52/4
Bagaradad	—	—	—	—	51/6	52/3	—	—	48/9	—	—	—	—	—	47/6	—	47/—	—	47/—	—
1st Class Roots	—	53/9	46/6	46/6	51/—	52/—	—	—	54/—	55/9	53/3	54/6	54/6	55/—	54/—	—	54/—	—	54/—	—
2nd "	—	53/6	—	—	47/—	—	—	—	—	—	49/6	—	—	—	—	—	55/9	—	53/—	—
3rd "	—	52/3	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	51/—	—
1st " Jugpokal	44/6	45/9	42/6	44/—	—	46/6	43/6	47/6	43/3	49/—	42/6	49/—	42/6	49/6	42/—	50/3	41/—	51/9	45/—	51/9
2nd "	40/6	44/6	40/—	41/3	—	45/6	41/6	46/9	40/3	48/3	40/9	48/3	41/3	49/—	—	49/6	39/—	51/—	43/—	—
Ain Bagar	—	42/6	—	—	—	45/6	—	—	—	—	41/6	47/—	—	—	40/—	—	39/—	—	—	—
Cheria	—	39/—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Ain Chilta	—	31/6	—	28/6	29/6	30/9	—	33/6	34/9	—	32/—	—	31/—	—	—	—	34/6	36/—	—	—
Hatri Chilta	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Milwa Chilta	25/3	26/3	25/—	25/—	24/3	27/6	25/6	26/3	25/—	27/6	24/6	28/6	25/—	29/6	25/—	20/6	23/9	31/3	21/—	31/3
Basola Bukni	—	21/—	18/6	19/3	21/—	23/—	—	21/6	18/6	22/6	19/6	22/9	19/6	23/—	19/6	23/9	18/3	26/—	18/6	26/—

Sassafras Oil. There has been no alteration in the value of this oil. In view of the abundant supplies which came forward during autumn and winter, present quotations are likely to remain unchanged, the eager demand preventing a decline of prices.

Satureja Oil. An oil which is perhaps derived from *Satureja montana*, and which resembles in its properties the oil of *Satureja cuneifolia* which has been examined by us¹⁾, is described by S. S. Pickles²⁾. The dry herb, which came from Trieste, yielded 1,64% oil with an odour resembling that of carvacrol, and possessing the following constants: d_{15}^{150} 0,9548, α_D — 1° 3', sol. in 2,7 vols. 70% alcohol. The oil contained 68,75% phenols, chiefly consisting of carvacrol.

Two distillates from the flowering herb of *Satureja montana* which were prepared by ourselves in the South of France some little time ago, may be included in the present reference. The oils were respectively of a lemon-yellow and a brownish colour; their odour reminded of thyme. Their characters were as follow: —

	Yield	d_{15}^{150}	α_D	n_{D200}	
Distilled at Barrême	0,23%	0,908	— 1° 42'	1,49488	{ Sol. in 8 vol. a. m. 80% alcohol
Distilled at Sault	0,15%	0,9194	— 4° 48'	—	{ Sol. in 1,5 vol. a. m. 80% alcohol

Both oils contained carvacrol, this body being represented in the Barrême oil by about 27% and in that from Sault by about 32%. We may add that *Satureja montana* is popularly known in the French Alps as "poivre d'âne".

Oil of Seseli Bocconi. L. Francesconi and E. Sernagiotto³⁾ have distilled from *Seseli Bocconi*, Guss. (*Bubon siculus*, Spr.; *Crithmum siculum*, Boccon; N. O. Umbelliferæ) 0,295% of an essential oil with sp. gr. 0,8475 (27°). Closer examination of the oil showed that *l*-pinene and β -phellandrene are to be regarded as its principal constituents. On a previous occasion the authors had described the distribution of the oil in the leaves, flower-stalks and stems of the plant⁴⁾. The root contains but little oil.

Shaddock (Grape fruit) Leaf Oil. There appear to be two varieties of the shaddock-tree (*Citrus decumana*, L.), a large-leaved shaddock, which is almost devoid of oil-cells, and a small-leaved variety. From the latter

¹⁾ Report October 1911, 109.

²⁾ Proceed. chem. Soc. 27 (1911), 285. See also Bull. Imp. Inst. 9 (1911), 388.

³⁾ Atti R. Accad. dei Lincei, Roma (5), 20, II. (1911), 481. Quoted from Chem. Zentralbl. 1912, I. 422.

⁴⁾ Atti R. Accad. dei Lincei, Roma (5), 20, II. (1911), 249. From a reprint kindly sent to us.

Brooks¹⁾ has obtained by distillation 1,7% of an oil with an agreeable aroma, possessing the following properties: d_{30}^{30} 0,8700, α_{D30} 22,90° (+ ?), n_{D30} 1,4644, ester v. 10, sol. in 70% alcohol. The oil contains 25% dipentene (m. p. of the tetrabromide 120°), 15% linalool (identified from its b. p. and from oxidation into citral) and 1% of an aldehyde reacting with bisulphite and possessing an odour of citral.

Spearmint Oil. The advancing tendency which has characterised this article since our last Report, and which still marks it, is chiefly traceable to the fact that the result of last autumn's distilling has brought universal disappointment, the expected yield not having been reached by a very long way. A few important producers have been compelled to purchase the annulment of their contracts for delivery. The demand was especially brisk in the United States, where, as is well known, spearmint oil is principally used for flavouring chewing gum. Our New York friends forecast unchanged high prices until the summer arrives, when a fall is not impossible, inasmuch as the high prices have induced many Western planters to extend their plantations considerably.

A spearmint oil of which the sample proved to be highly adulterated was recently offered to us from Russia.

Very interesting is the chemical examination of an authentic sample of American spearmint oil which has been carried out by E. K. Nelson²⁾. The oil, which has been distilled in Michigan from selected raw material, possessed the following characters: d_{25}^{25} 0,9290, α_{D25} — 52,16°, n_{D25} 1,4866, ester v. 12,4, ester v. after acet. 36,4, sol. in its own vol. 80% alcohol. It contained about 66% carvone. After eliminating the carvone, Nelson ascertained the presence in the oil of phellandrene (identified from the nitrosite) as well as of *l*-limonene, which he identified by conversion into the nitrosochloride and into carvoxime.

Some time ago Elze³⁾ had discovered dihydrocuminic acetate to be the carrier of the odorous principle of German spearmint oil. Singularly enough this ester was not present in the authentic American oil, which, however, contained the acetate of dihydrocarveol, an alcohol of which we had detected the presence in caraway oil several years ago⁴⁾. Nelson isolated dihydrocarveol from a fraction of the saponified oil which boiled between 100 and 115° (10 mm.). The alcohol reacted imperfectly with phthalic anhydride; it was found easier to separate it by heating to 125° with succinic anhydride. The dihydrocarveol was identified from its constants as well as by oxidising it into dihydrocarvone (m. p. of the semi-

¹⁾ Philippine Journ. of Sc. 6, A. (1911), 349.

²⁾ U. S. Dep. of Agriculture, Bureau of Chem. Circular No. 92.

³⁾ Chem. Ztg. 34 (1910), 1175; comp. Report April 1911, 106.

⁴⁾ Report April 1905, 20.

carbazone 200 to 201° when heating rapidly; m. p. of the oxime 88 to 89°). The acetic ester of dihydrocarveol had an odour of spearmint.

In addition to acetic acid and possibly also butyric, caproic or caprylic acids, the oil contained 0,1% of a solid acid, m. p. 182 to 184° which has also been observed by Nelson in several other samples of spearmint oil.

No fraction of the oil under examination had an odour of menthol.

According to K. Irk¹⁾, Hungarian spearmint oil constitutes a straw-coloured or faintly greenish-yellow liquid: $d_{40}^{15^{\circ}}$ 0,9375 to 0,9513, α_D — 44,38 to 49,85°, $n_{D20^{\circ}}$ 1,4899 to 1,4931, soluble in its own vol. of 80% and in one-half its own vol. and more of 90% alcohol. It contains from 62 to 71% *l*-carvone. The green herb yields 0,5278%, and the dry herb from 1,8530 to 2,4814% oil.

We have already previously reported on Hungarian spearmint oil (comp. Report April 1909, 85).

Spike Oil. At the commencement of March we found it necessary again to raise our prices, as the stocks of our excellent pure spike oil were approaching depletion and cannot be renewed before next August or September. We are therefore unable to execute large orders unless a suitable time for delivery is granted.

In our Report of November 1908, 115 we stated that spike oils of really good quality should be soluble in about 15 to 20 times their volume of 60% alcohol, if distilled by the method customary in France (*à feu nu*). Since then we have been privately informed that it has been observed that the degree of solubility of spike oil varies according to the origin of the oil. Oils from the Alps and from Provence are said to be soluble in 60% alcohol, and oils from the neighbourhood of Roche-Esclapon, a village in the Var, are said to dissolve even in 58% alcohol. On the other hand, the distillates from the Departments of the Bouches-du-Rhône, Vaucluse, Gard, Hérault and Aude, are said to be only rarely soluble in 60% alcohol. The differences are said to be due to variations in the conditions of the soil and the climate, and also to the method of distilling, distillation being often carried out without water and cooling. The matter is further complicated by the circumstance that, in order to increase the weight, the herb-cutters often mix with the spike other plants, such as *Satureja montana*, L., *Calamintha officinalis*, Moench, *Sideritis romana*, L., *Teucrium Polium*, L., &c., which, when the admixture is moderate, it is very difficult to pick out. With the object of checking the accuracy of these

¹⁾ Kiserletügyi Közlemenyek 14 (1911). From a reprint kindly sent to us. Also see Pharm. Zentralh. 52 (1911), 1111.

statements we caused a business-friend to make for us a collection of spike oils from various Departments. In the result we were unable to confirm the assertion that the degree of solubility depends upon the origin of the oil. On the contrary, our experience, as shown in the table printed below, is that generally speaking all the oils are soluble in the same degree, and that deviations occur independently of the locality of production. From this it may perhaps be inferred that the differences in solubility are actually determined only by the different methods of distillation or by the greater or less degree of care bestowed upon the collection of the raw material.

Origin	d_{150}	α_D	α_D of the initial 10%	acid v.	ester v.	Solubility in 60% alcohol
Basses-Alpes:						
La Palud de Moustiers . .	0,9040	$-2^{\circ} 12'$	$+1^{\circ} 30'$	0,6	10,0	in 6 vols. a. m.
Beynes près Mézel	0,9052	$-1^{\circ} 47'$	$+1^{\circ} 4'$	1,1	9,0	in 6 vols. a. m.
Les Mées	0,9070	$+0^{\circ} 15'$	$+3^{\circ} 30'$	0,4	7,5	in 6 vols. a. m.
Forcalquier	0,9071	$+0^{\circ} 24'$	$+4^{\circ} 0'$	0,8	14,1	in 20 vols. a. m.
Reillanne	0,9075	$-0^{\circ} 28'$	$+2^{\circ} 34'$	0,8	9,4	in 7 vols. a. m.
Vaucluse:						
Pertuis	0,9073	$+0^{\circ} 38'$	$+3^{\circ} 54'$	0,8	9,4	in 7 vols. a. m.
Bouches-du-Rhône:						
Jouques	0,9070	$+0^{\circ} 38'$	$+3^{\circ} 46'$	0,5	6,9	in 7,5 vols. a. m.
Drôme:						
Montségur	0,9138	$+3^{\circ} 38'$	$+5^{\circ} 26'$	0,8	7,5	in 14 vols. a. m.

Star Anise Oil. Since our last Report a change of importance has occurred in the position of the article, the primary cause of which was to be found in large sales of both Chinese and Tonquin oil, as a result of which the prices rapidly advanced by about 10 per cent. Next, the outbreak of the Chinese revolution afforded a further reason for giving a firm tendency to the market and, finally, when owing to the unsettlement of the political conditions the supplies from the interior were cut off, the quotations advanced to about 6/-. Some of the shippers in these circumstances pleaded *force majeure*, but opinions varied as to the justification of this plea. In any case, during the past few weeks the market has calmed down to this extent that offers are once more available. It is natural that for the present the quotations should still remain very high and it will depend upon the demand whether a further advance will occur. At the present high figures there have not, so far as we know, been any transactions of importance. From the other side the position is described as firm.

E. W. Mann¹⁾ attributes the imperfect solubility of certain star anise oils in 90% alcohol to some form of sophistication the true nature of which has been unable to determine; but which he surmises to have its source in cedar wood oil, because the distillation residues of the samples examined by him possessed a well-marked woody flavour not dissimilar to that of cedar wood oil, which was not perceptible in the residue of an oil of normal solubility. In our opinion any addition of this character can only have been a slight one, because cedar wood oil is somewhat strongly lævorotatory, and Mann's samples only showed rotations ranging from $\pm 0^\circ$ to a maximum of $-0^\circ 12'$. A sophistication of the kind suggested appears to us to be all the more doubtful, because we ourselves some years ago, and again recently, have observed readily-soluble star anise oils, but these were found to be adulterated with fatty oil, which was isolated by driving off the volatile fractions with steam, and was clearly identified by its insolubility in 95% alcohol, its high saponification value and the melting-point of the isolated fatty acids. The subjoined table shows the characteristics of our oils, both before and after rectification by steam, and of the distillation residues: —

	d_{20°	α_D	Sol. pt.	Sol. in 90% alcohol	Sap. v.	m. p. of the fatty acids
Original Oils	1) 0,9807	$-0^\circ 15'$	$+15,8^\circ$	Both insol. in 10 vols.	—	—
	2) 0,9800	$-0^\circ 9'$	$+15,5^\circ$		—	—
The same rectified	1) 0,9805	$-0^\circ 15'$	$+16,1^\circ$	in 2 vols. a. m.	—	—
	2) 0,9816	$-0^\circ 11'$	$+16^\circ$	in 3 vols. a. m.	—	—
Dist. residue	1) —	—	—	Both insol. in 10 vols. 95% alcohol	140,1	29 to 30°
	2) —	—	—		148,0	39°

Tansy Oil has also advanced in price. It is probable that there will be a further rise in the quotations, as there is only a little oil left over from the last crop.

Oil of Thuja plicata. From the leaves and branches of the Washington cedar (*Thuja plicata*, Lamb.), R. E. Rose and C. Livingstone²⁾ have obtained by distillation 1% of a pale yellow oil of the following characters: d_{20° 0,913, $[\alpha]_{D20^\circ}$ $-4,77^\circ$, n_{D20° 1,4552, acid v. 0,518, ester v. 2,28, ester v. after acet. 8,8. The oil was soluble in any proportion in 70% alcohol; 85% of the oil distilled between 100 and 110° (40 mm.) and consisted of

¹⁾ Perfum. and Essent. Oil Record 2 (1911), 273.

²⁾ Journ. Americ. chem. Soc. 34 (1912), 201.

α -thujone (m. p. of the tribromide 121 to 122°; m. p. of the semicarbazone 186 to 188°). The oil also contained from 3 to 5% *d*- α -pinene, which was identified by its constants as well as by the preparation of its nitroso-chloride. The authors further found the product to contain from 1 to 3% tanacetyl alcohol, which body was identified by its constants (b. p. 210 to 220; d_{250} 0,9266; $[\alpha]_{D250} + 29,8^\circ$; n_{D250} 1,46207), and which appears to occur in the oil in the form of an acetate. Fenchone was not detected.

As the authors only quote the paper of Brandel and Dewey¹⁾ on oil of *Thuja plicata*, it would appear that they have overlooked the work of Blasdale²⁾ and our own communication on the subject³⁾.

The oil obtained by us (yield 1,32%) from the air-dried leaves and branches gave the following constants: d_{150} 0,9056, $\alpha_D + 5^\circ 4'$, n_{D200} 1,45721, acid v. 0,8, ester v. 16,9.

Thyme Oil has remained very quiet. There have been plentiful arrivals of qualities rich in phenol, and the low prices have remained unchanged.

Toddalia Oil. The oil from the leaves of *Toddalia asiatica*, L. (Kurz) [*T. aculeata*, Pers.⁴⁾ according to the *Index Kewensis*] has been distilled in the Philippines⁵⁾ by Brooks. The yield was 0,08%, and the constants were as follow: d_{300}^{300} 0,9059, n_{D300} 1,4620. During cooling there was precipitated 18% of a substance with an odour reminding of camphor, and very liable to decomposition, which, when recrystallised from light petroleum, melted between 96,5 and 97°. A fraction of the oil which boiled over between 195 and 200° contained linalool, which was identified by oxidation into citral.

Trawas Leaf Oil. The leaves of *Litsea odorifera*, Valetton (N. O. Lauraceæ), a native of Java, are known in that island as *trawas* leaves and are in use as a popular remedy. According to van Romburgh⁶⁾, they yield an essential oil possessing the following constants: d_{150} 0,836 to 0,846, $\alpha_D - 0^\circ 10'$ to $- 7^\circ$ (in a 200 mm. tube). The principal fraction of the oil boiled at 233° (120 to 125° at 10 mm.). With semicarbazide it formed a semicarbazone, m. p. 116°, from which a ketone was regenerated. This was treated by van Romburgh with permanganate of potassium, from which resulted a ketone, m. p. 12° (b. p. 234°; d_{170} 0,829; m. p. of the semicarbazone 124°), which proved to be methylnonylketone. From the oxidation-liquid an acid $C_{10}H_{18}O_3$, m. p. 49°, was isolated. This was 2-ketodecylic acid, and, when oxidised with chromic acid and sulphuric acid, yielded suberic acid, while oxydation with sodium hypobromite

¹⁾ Pharm. Review 26 (1908), 248; comp. Report November 1908, 117.

²⁾ Journ. Americ. chem. Soc. 29 (1907), 539; comp. Report October 1907, 91.

³⁾ Report April 1909, 89.

⁴⁾ Comp. Gildemeister and Hoffmann, *The Volatile Oils*, p. 460.

⁵⁾ Philippine Journ. of Sc. 4, A. (1911), 344.

⁶⁾ Koninkl. Akad. Wetensch. Amsterdam. Meeting of 28. 10. 1911, p. 325. From a reprint kindly sent to us.

resulted in azelaic acid and carbon tetrabromide. The unsaturated ketone which is present in the oil must therefore be nonylene-1-methylketone. As it was found impossible, by recrystallisation, to split up the semicarbazone from the original oil into its constituents, the ketone mixture which was regenerated from it was brominated, with a methyl alcoholic bromine solution, when hardly any portion of it reacted except the unsaturated ketone¹⁾. After the saturated ketone had been distilled off the dibromide passed over at 204° (15 mm.). Upon the bromine being abstracted from the dibromide with zinc-dust and alcohol, there resulted a ketone, m. p. — 7°; b. p. 235°; $d_{11,50}$ 0,848; mol. refr. 52,47, calc. for $C_{10}H_{20}O$ ($\bar{r}_1$ 52,51²⁾).

The alcohols of the trawas oil were separated by a similar method, and proved to be 1-methyl-*n*-nonylcarbinol (α_D — 5° 40') and undecene-1-ol-10 (b. p. 233°; d_{100} 0,835). Methylnonylcarbinol was identified by oxidation into methyl-*n*-nonylketone; undecenol, when oxidised with chromic acid and sulphuric acid, yielded a ketone of which the semicarbazone had m. p. 113°; when oxidised with permanganate of potassium it yielded 2-ketodecyclic acid.

An oil of which a sample was sent to us from Java many years ago under the name of "trawas olie" may here be mentioned. Its behaviour was as follows: d_{150} 0,9127, α_D — 20° 12', n_{D20} 1,46377, soluble in 1,1 vols a. m. 80% alcohol; the diluted solution showed slight opalescence. The oil was rich in cineole, as was evident from its odour, which also reminded of cardamoms.

Turpentine Oil. The method of turpentine-production by the new "cup and gutter" system, which we have repeatedly described in detail. has, according to an American Journal³⁾, the disadvantage that the cups employed for collecting the balsam are often upset by hogs and other animals which scour the forest for food. Many of the earthenware cups, no matter how carefully they are handled, are lost by breakage, and, finally, a good deal of the turpentine oil is wasted by evaporation. All drawbacks, as well as the danger of fire, are said to be obviated by a new method in which the collecting-vessel and the tapping-place in the tree are connected in an air-tight manner. This is done by boring into the sapwood of the tree a hole of $2\frac{3}{8}$ inches diameter, and not too deep. From the centre of this hole two other holes, $\frac{3}{4}$ inch in diameter each, are bored steep upwards in a slanting direction, to the depth of a few

¹⁾ According to Lobry de Bruyn [Berl. Berichte 26 (1893), 272] bromine acts much more slowly upon methyl alcohol than upon ethyl alcohol, hence the former is to be preferred for brominating purposes.

²⁾ In this connection it should be borne in mind that possibly the ketone may still contain traces of saturated ketone which may be formed from the unsaturated ketone in the course of the treatment with zinc-dust.

³⁾ Scientific American 105 (1911), 383.

inches. The rough bark surrounding the central opening is smoothed down to admit of the opening being closed with a flat cover. This cover communicates by means of a hollow prop with a second cover placed at right angles to the first, and into this second cover a glass receptacle, holding about one pint, is screwed air-tight. The turpentine collects first in the $\frac{3}{4}$ inch holes, and flows thence through the wider hole and the hollow prop into the glass receptacle which, when full, is replaced by another. It is said that this new method possesses several advantages over those now in use. Among these, in addition to the avoidance of the disadvantages enumerated above, are the preservation of the trees, coupled with the possibility of tapping them for an unlimited period; the prevention of loss by running or evaporation and the avoidance of the costly and destructive process of preparing the drawing-surface by cutting.

It appears to us, at any rate at first sight, that the considerably higher cost-price of the glass receptacles and metal-parts as compared with the simple earthenware cups and tin-strips of the "cup and gutter" method, will be a disadvantage of the new process.

Numerous investigations, especially by French chemists, have shown the pinene of the Aleppo fir (*Pinus halepensis*) to be specially rich in pure *d*- α -pinene. On the other hand, Fernandez¹⁾ has found that the pinene from the Andalusian fir, which is identical with the Aleppo fir, is not quite identical with ordinary pinene. Unfortunately the abstract of Fernandez' paper before us gives no particulars of the constants of the pinene mentioned by him. He assumes the two pinenes to differ from each other because no nitrosites were obtainable from the Spanish pinene. When attacked by nitrogen tetroxide in the presence of acetic acid at 0°, a brownish-black body (probably an oxime) with a cymene-like odour was separated out. This body constituted about 55% by weight of the pinene used. The corresponding pinene nitrolpiperidine constituted a spongy, non-crystalline mass. With toluidine, Fernandez obtained high-boiling fluids which distilled over between 130 and 141° at 14 mm.; from the naphthylamines and the sulphanilic acid he was unable to obtain nitrolamines. The Spanish pinene only afforded 10% crystalline terpene.

In the abstract at our disposal several points are left obscure. It is to be regretted that Fernandez does not state the constants of Spanish fir oil. We are uncertain what Fernandez means by his crystallised terpene, — whether camphene, prepared from conversion from the pinene hydrochloride or direct from the oil, or whether terpene? The fact that with aromatic bases such as aniline (and certainly also with homologous bases) pinene nitrosochloride does not afford nitrolamines, but pinene and amidoazobenzene is, we should think, generally known.

¹⁾ Chem. Ztg. 35 (1911), 1152. From a lecture.

To our several notes¹⁾ on Greek turpentine oil from *Pinus halepensis* we are now able to add the result of an examination by Parry²⁾ who has found two authentic samples to possess the following characters:—

	I	II
$d_{15^{\circ}}$	0,8605	0,862
α_D	+ 36° 45'	+ 39°
$n_{D20^{\circ}}$	1,4690	1,4736
Commences to distil at . .	156°	156°
Fraction 156 to 160° . . .	70%	72%
α_D of 156 to 160° fraction	+ 37° 15'	+ 40°

In addition to the hydrocarbons *l*-pinene and sylvestrene, the presence of which in turpentine oil from *Pinus longifolia* we detected some time ago³⁾, H. H. Robinson⁴⁾, has found the oil to contain dipentene. Robinson is of opinion that possibly sylvestrene may not be present as such in the original oil, but that the oil may contain a hydrocarbon which, when treated with hydrochloric acid, yields a sylvestrene derivative, in the same way as a hydrochloride results from the treatment of pinene which by splitting off the latter yields camphene.

When the turpentine from the Douglas fir (*Pseudotsuga Douglasii*, Carr.) is distilled with steam under low pressure until all the turpentine oil has distilled over, there is left behind a clear, viscous yellow oil (Fir oil) which resembles the so-called pine oil from common turpentine. According to Walker, and also Teeple⁵⁾, this fir oil contains large proportions of terpineol. Benson and Darrin⁶⁾ have examined a sample of fir oil, and found it to possess the following constants: m. p. below — 40°, $[\alpha]_{D20^{\circ}}$ — 37,6°, $n_{D20^{\circ}}$ 1,4818; solubility in 70% alcohol 49 : 100, acid v. 1,55, sap. v. 11,1, iodine value 185. From its constitution and its behaviour under fractionation, as well as from the readiness with which terpine hydrate was formed when the sample was treated with 5% sulphuric acid, the authors conclude that at least one-third of the oil consists of terpineol, and that for many purposes it may be found to supply a substitute for pine oil.

Queysanne⁷⁾ has proposed a purity-test for turpentine oil based upon its miscibility with aniline, and this same principle was subsequently adopted

¹⁾ Report April 1905, 79; October 1905, 67; October 1909, 69.

²⁾ Perfum. and Essent. Oil Record 2 (1911), 210.

³⁾ Report April 1911, 116; October 1911, 93.

⁴⁾ Proceed. chem. Soc. 27 (1911), 247.

⁵⁾ Comp. Report November 1908, 125.

⁶⁾ Journ. Ind. Eng. Chem. 3 (1911), 818. Quoted from Journ. Soc. chem. Industry 30 (1911), 1407.

⁷⁾ Comp. Report April 1910, 115.

by Louise¹⁾ in testing turpentine oil. The experiments of Queysanne with lævorotatory French oil have been amplified by investigations conducted by Gallon²⁾. The samples of oil under examination possessed the following constants: d_{15}^0 0,8675 and 0,8682, n_{D25}^0 1,4668 and 1,4655, $\alpha_{D10}^0 + 40,32^0$ and $39,99^0$ respectively. The constants quoted in the second set of figures refer to another, but rather "older", sample of the same oil, the difference in age being shown in the somewhat slighter solubility of the "older" sample. But on the whole, the dextrorotatory oil was not so soluble in aniline as the lævorotatory sample which had previously been examined.

That the chemical testing of turpentine oil offers great difficulties is evident from the numerous publications on the subject. P. van der Wielen³⁾, who has been engaged in the investigation of this oil, proposes a modification of the sulphuric acid method. To 80 cc. sulphuric acid (d 1,698) in a flask of about 1 litre capacity, he adds 20 cc. of the oil under examination, and allows the mixture to stand for an hour under repeated shaking. After adding 300 cc. water the oil which has not been attacked is distilled over into a bottle with a graduated neck. The coefficient of refraction as well as the separation temperature of the solution in aniline are determined. It is also necessary to know the refraction of the original oil. According to van der Wielen, an addition of hydrocarbons⁴⁾ may be detected positively from the above data as well as from the quantity of oil which has not been polymerised by sulphuric acid. The author has examined by this method a large number of samples of turpentine oil as well as various substitutes and mixtures with benzene, hydrocarbons and carbon tetrachloride, and has collected the results in table-form.

For determining the evaporation-residue of turpentine oil, Herzfeld, and also Kollo⁵⁾ recommend the embedding of the platinum dish in a sand-bath, and the heating of the latter to 155^0 before filling-in the oil. In order to obviate the risk of explosion of the suddenly-generated vapour, a tin-ring is to be affixed below the rim of the dish. Wolff⁶⁾ has observed that when the dish is merely embedded in sand, the last particles of oil frequently creep over, and he obviates this trouble by surrounding the dish with a tin-cylinder about 2 inches in height and of a diameter exceeding that of the upper portion of the dish by nearly half an inch. This cylinder is stuck in the sand to a depth of about $\frac{1}{4}$ inch.

¹⁾ Comp. Report October 1910, 139.

²⁾ P. E. Gallon, *Sur la solubilité réciproque de l'essence de térébenthine dextrogyre et de l'aniline*. Bordeaux 1911. From a reprint kindly sent to us.

³⁾ Pharm. Weekblad 8 (1911), No. 35.

⁴⁾ By hydrocarbons the author apparently understands petroleum-hydrocarbons.

⁵⁾ Comp. Report April 1910, 116.

⁶⁾ Farbenzeitung 16 (1911), 2746. Quoted from Chem. Zentralbl. 1911, II, 1181.

In view of the increasing importance of the so-called wood turpentine, as a result of the scarcity of genuine turpentine oil, the U. S. Department of Agriculture has caused two of its chemists, Messrs. Veitch and Donk, to report, in the detailed manner customary with this Department, upon the present experience relating to the production, refining and uses of wood turpentine¹). The report deals in the first place with the production of the oil by the various processes in use: destructive distillation, steam-distillation, and extraction with volatile and non-volatile solvents. Of these, steam-distillation produces the most useful oil. The distillate obtained by the destructive process, that is to say the fraction which distils over up to 170° and which is also called "wood turpentine" is quantitatively too small in comparison with the oils of higher b. p. Moreover, it is much more difficult to remove the characteristic pine-tar odour of this product by refining, than is the case with the oil obtained by steam-distillation. The method of extracting with volatile solvents is still in its infancy, but several plants use the method of extracting with hot rosin at 200° , which extracts the oil from the chipped wood. The rosin yields the oil to a current of superheated steam which is passed through it, and is afterwards used again for extracting fresh batches of wood. There is also a method of extracting the oil and resin from the wood by boiling the latter with soda liquor and removing the oil from the liquor with a steam-current before the rosin acids are precipitated; the cellulose of the raw material being worked up for paper. Of course the residual wood from the steam-distillation or the extraction with volatile solvents can also be made into paper-pulp or used for dry distillation.

Great importance is to be attached to the next process of purifying and fractionating the crude distillate, for which purpose a column-still either working intermittently or continuously, should be used. The distillate resulting from the destructive process is first freed from phenols by means of alkali and then refined by steam-distillation. Generally speaking, insufficient care is bestowed upon this work, and apparently the distillate is not fractionated; hence "carbonisation wood turpentine" is not to be regarded as a first-class product, owing to the considerable proportion of high-boiling oils contained in it. The portions of this oil which distil over between 80 and 154° closely resemble rosin spirits; the fraction boiling between 154 and 180° constitutes the destructively-distilled wood turpentine. It contains pinene, dipentene and other compounds which also occur in part in rosin spirits. The higher-boiling oils, with b. p. exceeding 180° , are mixtures of pine-tar and rosin oils in indefinite proportions and are used as greases and solvents, in the manufacture of printers' inks, &c. The constitution of the crude product of the steam-distillation of light wood

¹) Wood turpentine, its production, refining, properties, and uses. U. S. Dept. of Agriculture, Bur. of Chemistry, Bulletin No. 144, 1911.

is very different from the above. As a rule it is collected in the following two or three fractions: wood turpentine proper, b. p. 150—160° up to 175—180°; light pine-tar oil, b. p. 170—180° up to 210—225°; heavy pine-tar oil, b. p. 180—190° up to 230—240°. The first fractions contain chiefly pinene, also camphene, limonene, dipentene, and cineole, and (in case of careless fractionation) more or less terpinene, borneol, and terpineol. The pine-tar oil portions contain, in addition to small proportions of the terpenes, chiefly terpineol, borneol and fenchyl alcohol. A great many attempts have been made to free wood turpentine from its characteristic objectionable odour. It is true that the very first fractions of the steam-distilled oil have a pure odour, but the yield is too small to justify the rejection of subsequent fractions to make it practicable to collect them by themselves, and perhaps to disregard the succeeding fractions. Special experiments carried out by the Department have shown that the unpleasant odour attaches principally, although not entirely, to the higher boiling portions which are still included in the low-boiling fraction, and special importance is to be attached to the removal of these by carefully-conducted fractionation. When this is done, however, wood turpentine very closely resembles genuine turpentine oil, both in its odour and in its constitution. The following table shows the properties of the usual commercial turpentine oils: —

Constants	Wood turpentine oil		
	Gum Turpentine oil	Steam-distilled	by destructive process
d_{20}^0	0,8617 to 0,8889	0,859 to 0,915	0,857 to 0,898
α_{D20}^0	—34,8° " +29,6°	+16,5° " +36,14°	+34,4° " +77,6°
n_{D20}^0	1,4684 " 1,4818	1,4673 " 1,4755	1,4666 " 1,4810
Initial distilling point (uncorr.)	154 " 159°	153 " 177°	150 " 169°
Distilling below 170°	73 " 99%	0 " 95%	0 " 93%
Distilling below 185°	88 " 99%	20 " 98%	61 " 97%
Iodine value according to Wijs	350 " 400	300 " 362	300 " 398
Acid v.	0,140 " 0,286	0,080 " 0,312	0,028 " 0,246
Sap. v.	2,44 " 8,60	1,06 " 8,75	0,65 " 4,32
Color (Lovibond)			
for yellow	0,7 " 2,5	0,5 " 10,0	0,4 " 4,5
for red	0,0 " 0,5	0,2 " 1,4	0,0 " 0,8

The iodine-value is regarded as of significance, inasmuch as it indicates the proportion of heavy oil; but similar conclusions may be drawn from the saponification-value. Comparison of the crude with the rectified oils and their constants shows that rectification, as it is carried out in practice up to the present, hardly improves the quality, but only produces a distillate of a paler colour. The authors of the report go into full details on the subject of the experiments in fractionation which they conducted on a large scale, both in a simple and in a column still with direct steam. So far the record of the working showed no considerable difference

in the action of the two stills, but it is said that no definite judgment can yet be formed. So far as the evaluation of an oil-fraction in respect of its value as good, low-boiling wood turpentine is concerned, neither the often varying temperature of the steam which passes over, nor the specific gravity of the oil-particles is conclusive, but rather, according to practical experience, the respective proportions of oil and water in each fraction that distils over. The higher the proportion of oil, the more closely the properties of the oil approximate those of a good wood turpentine. When the total-distillate contains 55% oil or more, the proportion of good oil boiling below 170° is 90%; when the total proportion of oil ranges from 55 to 30%, renewed steam-distillation is needed in order again to obtain a light portion containing 55% of good oil (as before). Finally when the oil-content of the total distillate falls below 30%, it consists entirely of high-boiling oils, which it is unnecessary to try to work up for oils with b. p. below 170° .

With a view of deciding the important question to what extent the various wood turpentines could be used in the manufacture of paints and varnishes side by side with gum spirits, several varnishes were prepared with four samples of commercial oils, consisting of one sample each of guaranteed pure oil from gum of a steam-distilled wood turpentine and two wood turpentines prepared by the destructive process and subsequently washed with soda and steam-distilled. In connection with these experiments it is expressly stated that, apart from one of the two samples last-mentioned, the wood oils contained large proportions of heavy oil from which they derived a pronounced odour, and which caused the varnishes prepared with them to dry more slowly than usual. It is evident that varnishes prepared with oils of this description must give less satisfactory results than when a well-rectified oil had been used. From each of the four samples two kinds of varnishes were prepared, a coach finishing varnish and a piano varnish, with a view of testing their qualities under different atmospheric influences. We are unable to quote here the very detailed reproduction of the reports of the numerous firms which instituted these tests; partly preparing the varnishes themselves, and partly using them only. The disagreeable odour and the irritant action of the wood turpentine are generally commented upon; on the usefulness of the varnishes themselves the opinions differ. On the other hand the producers of wood turpentine of course claim that their productions are entirely suitable for the manufacture of paints, varnishes, &c.

We are now able to complete, on the authority of an American report, the particulars given in our last Report (p. 92) concerning the output of the various products of the American wood-distilling plants¹⁾. From this

¹⁾ Oil, Paint and Drug Reporter 80 (1911), No. 26, p. 9.

it appears that in the year 1910 30 plants were engaged in the distillation of soft woods, principally yellow pine, together with small quantities of Norway pine and Douglas fir. The plants turned out an aggregate of 192442 cords soft wood, as compared with 115310, 99212, and 62349 cords in the years 1909 to 1907 — a proof of the increasing importance of the wood-turpentine industry.

In view of the large imports of Finnish and Swedish pine-tar oil into France, which are probably due principally to the prohibitive customs duty upon pure turpentine oil, a brief essay by Blarez and Vèzes¹⁾ on the properties of pine-tar oil from Northern Europe should be very useful to all those in France who are interested in oil of turpentine. In making comparisons between genuine turpentine oil and pine-tar oil, the following general characteristics of the latter chiefly deserve consideration: its very marked empyreumatic, unpleasant odour; its lower sp. gr. ($d_{25} 0,8520$ to $0,8570$); its lesser degree of volatility, a property which varies considerably in different samples; its higher co-efficient of refraction ($n_D 1,4700$ to $1,4800$) which also varies in the separate fractions, and, finally, its dextrorotation ($\alpha_D +4$ to $+5^\circ$). Other points of difference are the readiness with which pine-tar oils dissolve in aniline, and Herzfeld's reaction. Mixtures of pine-tar oil with turpentine oil from the Landes may be detected and quantitatively estimated most readily by determining the rotation and by the temperature at which a mixture with known quantities of aniline separates.

To detect the presence of pine-tar oil in turpentine oil, Herzfeld has recommended the shaking of the latter with an equal volume of solution of sulphurous acid (yellow coloration denotes the presence of pine-tar oil; comp. Report April 1905, 78). Herzfeld has also recommended another test, consisting in pouring the oil under examination over a piece of caustic potash, when the presence of pine-tar oil is revealed by the caustic potash rapidly assuming a brown colour (Report April 1910, 110). H. Wolff²⁾ has modified the last-named test by shaking up 0,5 to 1 cc. potash liquor ($d 1,3$) with the oil, warming the mixture on the water-bath for 2 to 5 minutes, and then adding 3 cc. water to separate the emulsion. Pine-tar oil causes the aqueous layer to assume a brown colour, turpentine gives none, or only a very faint colour. Wolff gives two more tests for pine-tar oil which we quote below, without expressing an opinion on their value: —

1. 5 cc. oil are brought to boiling with 5 drops nitrobenzene, when 2 cc. 25% hydrochloric acid are added and the mixture is kept

¹⁾ *Sur l'essence de pin des pays du Nord de l'Europe*. Bordeaux 1911. From a reprint kindly sent to us.

²⁾ *Farben Ztg.* 17 (1911), 21, 78. Quoted from *Chem. Ztg. Repert.* 36 (1912), 64.

boiling for 10 seconds more. Pine-tar oil turns brown, the hydrochloric acid brown to black. Turpentine oil gives much paler tints.

2. To a mixture of 4 cc. each of ferric chloride (1:2500) and potassium ferricyanide solution (1:500) add from 2 to at most 10 drops of the oil to be tested and shake the whole vigorously. Pine-tar oil will rapidly give a copious precipitate of Prussian blue, whereas turpentine oil only gives a perceptible separation of that body after the lapse of some hours.

C. Piest¹⁾ proposes the following reaction to effect the same object: —

Shake in a test-tube 5 cc. acetic anhydride with 5 cc. turpentine oil, and add 10 drops concentrated hydrochloric acid while shaking and cooling. When the mixture has cooled down completely add with shaking, 5 drops more of concentrated hydrochloric acid; this will cause the liquid to become warm and to make a clear solution. Turpentine oil then remains water-white, pine-tar oil turns black.

In every case the turpentine oil, whatever its origin, should be distilled before being tested.

In commenting upon a paper by Grimaldi on the detection of camphene in light resin oil and in other oils²⁾, we took exception, in a footnote, to the use by Grimaldi of the designation "turpentine-essence" for light resin oil, because, especially in translating, the term encourages confusion with turpentine oil. In a letter which he has addressed to us Grimaldi disowns the authorship of the term, and declares that he has taken it from a paper by Valenta³⁾, who may possibly have borrowed it himself. It is also necessary, Grimaldi observes, to differentiate between turpentine essence, and light resin oils or pinoline; the last-named being that product of the distillation of colophony which passes over at up to about 230°, whereas "turpentine essence" constitutes the most volatile fractions of that distillation, boiling over between 160 and 170°.

We admit that in our footnote we drew no such sharp distinction between the two distillates, as we did in previous Reports⁴⁾. That, anyhow, was not our principal object, which was chiefly to enter a protest against the use of the name "turpentine essence" as inappropriate, without, however, expressing an opinion on the authorship of the term. And on the point to which we attach the most importance, Grimaldi agrees with us.

Valerian Oil. We always have at our disposal considerable quantities of superior oil of our own distilling and shall be pleased to submit special offers when quantities of some importance are in question. This article

¹⁾ Chem. Ztg. 36 (1912), 198.

²⁾ Report April 1911, 118.

³⁾ Chem. Ztg. 29 (1905), 807; Report October 1905, 70.

⁴⁾ As, for example, Report October 1905, 71; April 1908, 105.

has acquired a wide circle of regular customers within the past decade or two, especially among tobacco manufacturers.

Vetiver Oil. We have always at our disposal a considerable stock of excellent oil of our own distilling, and we are therefore in a position to pick out from the arrivals of vetiver root (which are notoriously irregular) those parcels which are richest in perfume and most suitable for our purposes. The quality of our distillate is unapproached, and in the preparation of really fine perfumes its employment is indispensable. Réunion vetiver oil continues to be firm. It is true that the exports in the year 1911 reached 975 kilos, and are therefore but little below those of the previous year, when they amounted to 1007 kilos, but reports dated December 31st state that there are no further supplies in the island. If the production should really be restricted, at it is said will be the case, the prices would of course be correspondingly affected. But so many contradictory statements have obtained currency concerning those articles of produce from Réunion which are of interest to us, that as a matter of course we regard the above report with the same scepticism as the rest.

The experiments in cultivation which have been carried out at Buitenzorg with the *Akar wangi* plant, the non-flowering variety of *Andropogon muricatus* which occurs in Java¹⁾, have shown that when grown in the shade the production of root is unfavourably affected, whereas repeated cutting of the plant has a favourable effect upon the development of the roots.

Walnut Leaf Oil. As, generally speaking, very little is known of the properties of walnut leaf oil, the following note on two oils, one of which was distilled by us at Miltitz and the other at Barrême, may be of interest. The distillates were of an olive-brown colour and possessed the characteristic odour of walnut-leaves. At about 10° they formed semi-solid, butter-like masses, which melted at about 20°. From the solutions in 90% alcohol large quantities of paraffin separated out, which after repeated recrystallisation from alcohol gave m. p. 61 to 62°. The constants of the oil are shown in the table below, and in connection with

Distilled at	Yield	d ₃₀ °	α _D	n _D 25°	Acid v.	Ester v.	Ester v. after acet.
Miltitz	0,014 %	0,9137	± 0°	1,49657	9,3	27,0	—
Barrême							
83% Principal oil	0,0072%	0,9174	— 17° 36'	1,49177	3,7	9,3	—
17% Water oil . .	0,0015%	0,9231	— 16° 12'	1,49366	4,7	9,7	—
100% Total oil . .	0,0087%	0,9185	— 17° 0'	1,49215	—	—	98,5

¹⁾ Jaarb. dep. landb. in Ned.-Indië, Batavia 1910, 48.

these figures it should be stated that we examined, of the Barrême oil first the distillate which had separated out directly in the receiver, next the oil obtained by extracting the distillation-water with ether, and lastly the total oil as represented by pouring together the two fractions.

It will be noticed that there are certain differences between the Miltitz and the Barrême oils, chiefly expressed in the optical behaviour.

Oil of Watermint. According to K. Irk¹⁾, Hungarian oil of *Mentha aquatica* possesses the following constants: d_{40}^{150} 0,9603, $\alpha_{D200} + 22,73^\circ$, n_{D200} 1,4900, sol. in 0,5 vols. of 90% alcohol. The oil is of a dark straw colour and possesses an agreeable odour reminding of pennyroyal. In its constants the oil shows a marked difference from an oil from Spanish herb described by Schimmel & Co.²⁾.

Wintergreen Oil, Indian. From 3,3 kilos of the leaves and stalks of *Gaultheria punctata*, Bl. (*G. fragrantissima*, Wall., comp. our last Report, p. 96) there was obtained at Buitenzorg³⁾ 23 cc. of oil with a density of $d_{200} 1,175$, $\alpha_D + 0^\circ$; sap. v. 234 (after 1 hour), 289 (after 2 hours), 357 (after 3 hours), 360,6 (after 4 hours), corresponding to 97,9% methyl salicylate.

The leaves and stalks of *Gaultheria leucocarpa*, Bl. (880 grams) have also been distilled, yielding 3 cc. oil. Sap. v. after 2 hours 332.

Wormseed Oil, American. American wormseed oil still remains scarce and dear and appears inclined at the very least to maintain its present level of value.

Our New York branch reports that it is extremely difficult to procure trustworthy data concerning the crop from the growing districts in Maryland, but the result is estimated not to exceed one-half of the average of previous years.

Wormwood Oil. Our New York friends report that the result of the American crop has fallen far below the original estimate and that, owing to the unfavourable climatic conditions, the contracts for delivery which had been concluded before the beginning of the distilling season have only been carried out to the extent of about 50 per cent. The prices have remained at their previous level, and would certainly have advanced considerably if the demand had not given way to an appreciable extent. This last statement is confirmed by our own experience of the American wormwood oil trade. This stagnation in the demand is doubtless in part attributable to the fact that in the European market the German wormwood oil distilled by ourselves is so popular that it would be preferred

¹⁾ Kiserletügyi Közlemenyek 14 (1911). From a reprint kindly sent to us. Also see Pharm. Zentralh. 52 (1911), 1111.

²⁾ Schimmel's Bericht, October 1889, 55; Gildemeister and Hoffmann, *The Volatile Oils*, p. 654.

³⁾ Jaarb. dep. landb. in Ned.-Indië, Batavia 1910, 47.

to American oil owing to its lower price alone, if for no other reasons. In respect of quality our German oil fulfills the most exacting requirements, and the employment of a more expensive quality is therefore merely a luxury. Our plantations have stood the winter well and will no doubt this year again produce sufficient oil for our requirements.

We hear that there is some intention of prohibiting entirely the consumption of absinth in France, and that a Bill to this effect is to be introduced before long in the Chamber of Deputies.

Xanthoxylum Oils. E. M. Holmes¹⁾ states that under the name of "Japanese pepper" a fruit has recently made its appearance upon the English market which is distinctly different from the fruit of *Xanthoxylum piperitum*, D. C., (usually known as Japanese pepper) and which no doubt really belongs to the species *X. alatum*, Rox.²⁾. According to an article by Umney which constitutes an amplification of the note by Holmes, the oil distilled from the above-named fruit was pale yellow in colour and had an odour resembling a mixture of lime and nutmeg; d_{20}^{20} 0.889, n_D^{20} — 23°. After standing for a few days crystals of stearoptene separated in the form of long, white needles, m. p. 80°; for the rest the oil was found to consist chiefly of terpenes, boiling between 170 and 200°. Umney believes the oil to be identical with one previously examined by J. Stenhouse³⁾. It is true that the latter stated that his oil was obtained from the fruit of *Xanthoxylum piperitum*, but according to Holmes, Stenhouse erroneously referred to the fruit from which his oil was prepared as *Xanthoxylum piperitum*. In reality it was that of *X. alatum*, a circumstance to which Hanbury had already previously drawn attention.

We may add to the above that in our Report of October 1910, 147, we gave detailed particulars of an oil distilled by us from the fruit of *Xanthoxylum alatum*, Roxb., a fact which has been completely overlooked both by Holmes and by Umney. In the present Report (see next page) we refer to a further examination of our oil by Semmler and Schossberger, from which it appears that the crystals which are separated from the oil (the "xanthoxyline" of Stenhouse) agree with phloracetophenone dimethyl-ether, while the terpenes ("xanthoxylene") are possibly identical with *l*-sabinene. It is probable that Holmes and Umney are correct in their assumption that the parent-plant of the oil examined by Stenhouse was *X. alatum* and *X. piperitum*, inasmuch as the constituents of the oil found by Stenhouse clearly point to *X. alatum*. Moreover, citral, which is a characteristic constituent of the oil of *X. piperitum*, and the presence of which is expressed in the odour of that oil, was absent, both from the oil obtained by us and from that distilled by Umney.

¹⁾ Perfum. and Essent. Oil Record 3 (1912), 37.

²⁾ These fruits are known in Japan as "Fuyu Sansho", i. e. "Winter Sansho", the designation "Sansho" being applied exclusively to the fruit of *X. piperitum*.

³⁾ Pharmaceutical Journ. l. 17 (1357), 19; Liebig's Annalen 104 (1857), 236.

The fruit of *X. piperitum* had been distilled by us many years previously and at that time (Report October 1890, 61) we also made a brief reference to the oil. A small sample of the fruit distilled at that time was still available and this we have again submitted to botanical examination, as a result of which we have confirmed its derivation from *X. piperitum*.

The oils obtained from *Xanthoxylum Aubertia*, D. C., and from *X. alatum*, Roxb., to which we have briefly referred in previous Reports¹⁾, have been thoroughly investigated by Semmler and Schossberger²⁾. They found the first-named oil to contain an aliphatic terpene, related to ocimene and alloocimene, and possessing the following properties: d_{200} 0,8248, $\alpha_D + 30^\circ$, n_D 1,49775. The high-boiling fractions of the oil contained a hitherto unknown, monocyclic sesquiterpene, to which the authors gave the name of evodene (b. p. 119 to 123° at 9 mm.; d_{200} 0,8781; $\alpha_D - 58^\circ$; n_D 1,49900). Semmler and Schossberger also showed the oil to contain from 40 to 60% methyleugenol, which they identified from its oxidation-product, veratric acid (m. p. 180 to 181°). After being heated with amylalcoholic potash liquor the refraction of the methyleugenol-fraction was considerably higher than before, from which follows that the oil contains methyleugenol and not methylisoeugenol. The fractions with the highest b. p. contained phloracetophenone dimethylether³⁾ a body of which the presence in oil of *Blumea balsamifera* was demonstrated in our laboratory some time ago⁴⁾.

In the oil of *Xanthoxylum alatum* the authors discovered a terpene which they call xanthoxylene⁵⁾, but which is perhaps identical with *l*-sabinene. This terpene yields a monohydrochloride, b. p. 83 to 87° (10 mm), d_{200} 0,959, $\alpha_D - 11^\circ$, n_D 1,4824; reduction of the latter with sodium and alcohol giving rise to a hydrocarbon $C_{10}H_{18}$ with the following constants: b. p. 52 to 58° (9 mm.), d_{200} 0,8275, $\alpha_D - 17^\circ$, n_D 1,4582. When ozonised, xanthoxylene forms a ketone of which the semicarbazone has b. p. 123° , whereas the m. p. of the sabinene ketone semicarbazone is 141° . Other constituents of the oil are phloracetophenone dimethylether and also perhaps cuminic aldehyde. The phloracetophenone dimethylether separates out from the oil at ordinary temperature in the form of a solid mass. This ether was characterised by its monobromide (m.p. 187°), its methyl derivate (m.p. 103°), and its acetyl derivate (m. p. 107°).

Ylang-Ylang Oil. Generally speaking the trade in ylang-ylang oil has been exceedingly flat, although the regular supplies of our "Sartorius"

¹⁾ Report April 1907, 105; October 1910, 127.

²⁾ Berl. Berichte 44 (1911), 2885.

³⁾ As regards characterisation see below.

⁴⁾ Jonas, Report April 1909, 147.

⁵⁾ The name "Xanthoxylene" has already been introduced by Stenhouse on a previous occasion, obviously for the same terpene. [Pharmaceutical Journ. I. 17 (1857), 19; Liebigs Annalen 104 (1857), 235; see also previous page.

brand, owing to their exquisite quality, have not been difficult to place, and our stocks in warehouse therefore never exceed a few original cases. It is true that the cheap Réunion oils, as has already been frequently pointed out by us, cannot approach the best reputed Manila brands in respect of quality, but it is nevertheless not surprising that French consumers in particular should evince a steadily-growing interest in this new product of the French Colonies. To this must be added the general tendency to buy low-priced goods, although as a matter of fact this tendency is wholly misplaced in the case of such fine products as ylang-ylang oil. The shipments of ylang-ylang oil from Réunion have declined from 2363 kilos in 1910 to 856 kilos in 1911, but in view of the enormous stocks which have been carried over from the year 1910, this decline has had no effect whatever upon the market-value.

In connection with an incident which has occurred in England we again take this opportunity to place upon record the fact that the sale of the "Sartorius" brand is entirely controlled by us, and that the brand is legally protected in all civilized countries.

An article by B. T. Brooks¹⁾ deals with the fluctuations in the market-values of ylang-ylang oil. He ascribes the fall in the prices mainly to the ever-increasing over-production, a fact upon which we have also laid stress on several occasions. Ten years ago, when the prices rose as a result of the political disturbances in the Philippines, the planting of ylang-ylang trees was quickly taken up in many localities, especially in Java, Jamaica, Bangkok, Tonquin, Nossi-Bé, Mayotte, and the Comoro Islands. The oils distilled in all these localities, however, are only of secondary quality and cannot compete with the first-class Philippine oils. As we have regularly reported on the production of ylang-ylang in the several countries named, this short reference to Brooks's article will be sufficient, especially because he bases himself chiefly upon our statements and upon those of Roure-Bertrand Fils.

Three years ago²⁾ we reported on an ylang-ylang oil which had been obtained by Bacon by the extraction method and of which the odour differed somewhat from that of the distilled oil. Bacon explained this difference by the presence of compounds very liable to decomposition which were destroyed in the process of steam-distillation. In order to discover to what extent ylang-ylang oil undergoes a change when heated with water, Brooks³⁾ heated a mixture of 5 grams of the oil with 15 cc. water on an oil-bath to a temperature of from 105 to 120° for 5 hours. At the end of that time the saponification value of the oil showed a drop

¹⁾ Philippine Journ. of Sc. 6, A. (1911), 355.

²⁾ Report October 1909, 131.

³⁾ Philippine Journ. of Sc. 6, A. (1911), 349.

of from 2 to 4 units. Brooks seeks to explain the differences in quality between ylang-ylang oils of the first and of the second class by a slight decomposition of the esters during the distilling of the flowers.

Two ylang-ylang oils which had been received by the firm of Roure-Bertrand Fils¹⁾ from Mayotte showed the following differences in constants: d_{150} 0,9594 and 0,9651, α_D — 53°56' and — 45°16', acid v. 1,3 and 1,4, ester v. 129,7 and 131,6, ester v. after acetylation 167 and 180,8, soluble in 1 vol. 95% alcohol, cloudiness ensuing when more alcohol was added. A third sample gave the unusually low optical rotation of — 4°4'.

Zedoary Seed Oil. It has not yet been possible to procure supplies of this oil, but consumers appear to have reconciled themselves to the lack of the article, for the demand has entirely ceased.

New Essential Oils.

Oil of *Aframomum angustifolium*. From the seed of a species of cardamoms indigenous in German East Africa, of which a sample had been sent to us from Usambara, we obtained by distillation 4,5% of a colourless oil possessing the following characters: d_{150} 0,9017, α_D — 16°50', n_{D20} 1,46911, acid v. 0,4, ester v. 4,2, sol. in 6 vols. a. m. 80% alcohol. So far as aroma is concerned it cannot compare with Ceylon cardamom oil, and owing to its high cineole-content it reminds rather of cajuput oil. Unfortunately the quantity of oil placed at our disposal was too small to enable us to estimate its constitution with any exactitude. Botanical examination of the entire fruit showed that the seed was derived from *Aframomum angustifolium*, K. Schum.²⁾ (N. O. Zingiberaceæ), a plant which occurs also in Madagascar and in the Seychelles Islands.

The Cameroon-cardamoms³⁾, which yield an oil similar in every respect to the above, and which also closely resemble the Usambara-fruit in appearance, are (according to a special definition made by our authority, Dr. Giessler) derived from another species, viz., *Aframomum Daniellii*, K. Schum. (*Amomum Daniellii*, Hook. f.). Sadebeck's⁴⁾ assertion that

¹⁾ Berichte von Roure-Bertrand Fils, October 1911, 43.

²⁾ According to K. Schumann's monograph on the Zingiberaceæ (Engler's *Pflanzenreich*, Part 20), the following are synonymous: *Amomum angustifolium*, Sonnerat, *A. madagascariense*, Lam., *A. nemorosum*, Boj. and *A. sansibaricum*, Werth. This nomenclature does not quite agree with the *Index Kewensis*, but the latter is no longer authoritative so far as concerns the matter here at issue.

³⁾ Comp. Gildemeister and Hoffmann, *The Volatile Oils*, p. 319.

⁴⁾ Sadebeck, *Kulturgewächse der deutschen Kolonien* (1899), p. 171.

the parent-plant of the Cameroon-cardamoms is *Amomum angustifolium*, Sonnerat, is incorrect, and the same applies to the statement in a notice on the cardamoms of tropical West Africa by D. Hanbury [*Pharmaceutical Journal* III. 2 (1872), 642] in which *Amomum Daniellii*, Hook. and *A. angustifolium*, Sonnerat are said to be identical.

Pharmacopœias.

The British Pharmaceutical Codex 1911.

A new Edition has appeared of the British Pharmaceutical Codex, which was first published by the Pharmaceutical Society of Great Britain in the year 1907. As the Codex deals with a number of articles pertaining to our trade, we took occasion at the time to comment upon these articles in our Report¹⁾. Unfortunately, our criticism has not had the result at which we aimed, for upon perusing the new Edition we observe that many erroneous statements have been transferred into it from the first Edition, although we also notice that numerous mistakes have been corrected. As the Codex is only a guide for pharmacists, and has no official force, we forbear, as regards the majority of articles to be quoted, from useless repetition, and will limit ourselves in the present review to the consideration of changes and amplifications, referring for the rest to our previous criticism. The above applies specially to any incorrect data which have been incorporated into the new from the old Edition, and which for that reason are not again criticized here. Similarly we refrain from mentioning articles in which no alterations have been made. None of the oils and preparations mentioned in the first Edition have been omitted from the second, while citronella oil has been newly added.

Ajowan Oil (*Oleum Ajowan*). $d_{15,50}$ 0,917 to 0,930¹⁾.

¹⁾ The minimum limit is too high; in the first Ed. it was given correctly as 0,900.

Anethol. $\alpha_D \pm 0^\circ$.

Anise Oil, Star Anise Oil (*Oleum Anisi*). d_{200} 0,975 to 0,990; α_D lævorotatory, up to -2° , occasionally slightly dextrorotatory; m. p. usually about 17° .

Bay Oil (*Oleum Pimentæ Foliorum*). $d_{15,50}$ 0,945 to 0,975¹⁾; α_D slightly lævorotatory, up to -6° ; phenol-content 40 to 65%.

¹⁾ The maximum limit is too low, and should be raised to at least 0,985.

¹⁾ Report April 1908, 134.

Bergamot Oil (*Oleum Bergamottæ*). $\alpha_D + 8$ to $+ 20^\circ$, occasional higher; evaporation residue 5 to 6%¹).

¹) The minimum limit should be reduced to 4.5.

Bitter Almond Oil (*Oleum Amygdalæ amaræ*). The oil containing hydrocyanic acid is now incorporated in lieu of the oil free from hydrocyanic acid. Colourless¹); $d_{15.50}$ 1,045 to 1,060; $\alpha_D \pm 0^\circ$; b. p. 179° ; sol. in any proportion in 90% alcohol. The natural oil may contain from 4 to 5% hydrocyanic acid; oil to be used for medicinal purposes should contain from 2 to 4% hydrocyanic acid. Test for the absence of chloride and nitrobenzene.

¹) Bitter Almond Oil assumes a yellowish colour with age.

Cajuput Oil (*Oleum Cajuputi*). $d_{15.50}$ 0,919 to 0,930; α_D lævorotatory up to $- 4^\circ$.

Camphor (*Camphora*). M. p. 175 to 179° .

Camphor Oil (*Oleum Camphoræ essentielle*). $d_{15.50}$ after removal of the safrol about 0,960. Heavy camphor oil containing safrol has $d_{15.50}$ 1,000 to 1,025; light camphor oil has $d_{15.50}$ 0,890 to 0,920 and $\alpha_D + 16$ to $+ 30^\circ$. As in the first Edition, it is again correctly stated that no definite standards can be given concerning its properties.

¹) The rotation is often considerably lower than 16° .

Caraway Oil (*Oleum Carui*). $\alpha_D + 70$ to $+ 82^\circ$; carvone-content 45 to 60%.

Cassia Oil (*Oleum Cassiæ*). $d_{15.50}$ 1,055 to 1,070; lead test¹).

¹) Notwithstanding all pains taken to procure oils which answer to this test, it is found impossible to do so.

Cedar Wood Oil (*Oleum Cedri*). $d_{15.50}$ 0,940 to 0,950¹); $\alpha_D - 30$ to $- 45^\circ$.

¹) For the maximum limit 0,961 would be a more correct value.

Chamomile Oil, German (*Oleum Matricariæ Chamomillæ*). $d_{15.50}$ 0,930 to 0,940¹).

¹) The sp. gr. ranges from 0,924 to 0,945.

Cinnamon Oil, Ceylon (*Oleum Cinnamomi*). $d_{15.50}$ 1,000 to 1,030¹); cinnamic aldehyde content about 55 to 65%²).

¹) The sp. gr. of normal Ceylon cinnamon oil ranges from 1,023 to 1,040.

²) Normal oil contains from 65 to 75% cinnamic aldehyde. Comp. Report October 1910, 35.

Citronella Oil (*Oleum Citronellæ*). Nearly colourless¹) or pale yellow $d_{15.50}$ 0,900 to 0,920 (for Java oil not below 0,885); α_D usually between 0 and $- 15^\circ$; sol. in 3 to 10 parts 80% alcohol without turbidity. Total geraniol in Java oil 80 to 90%, in Ceylon oil 55 to 65%.

¹) Ceylon Citronella Oil is generally yellow to yellowish brown.

Clove Oil (*Oleum Caryophylli*). $d_{15.50}$ 1,047 to 1,065; α_D lævorotatory up to $- 1^\circ 30'$; sol. in 3 vols. 70% alcohol.

Copaiba Oil (*Oleum Copaibæ*). $d_{15.50}$ 0,896 to 0,910.

Coriander Oil (*Oleum Coriandri*). $\alpha_D + 8$ to $+ 14^\circ$, occasionally lower¹⁾.

¹⁾ We have never observed pure oil with α_D lower than $+ 8^\circ$.

Cubeb Oil (*Oleum Cubebæ*). $d_{15,50}$ 0,910 to 0,930; $\alpha_D - 25$ to $- 40^\circ$.

Dill Oil (*Oleum Anethi*). $d_{15,50}$ 0,900 to 0,915¹⁾; $\alpha_D + 70$ to $+ 80^\circ$, sol. in 3 vols 90% alcohol.

¹⁾ The minimum limit is too high; it should be 0,895.

Eucalyptus Oil (*Oleum Eucalypti*). $d_{15,50}$ 0,910 to 0,930.

Fennel Oil (*Oleum Fœniculi*). $d_{15,50}$ 0,960 to 0,990¹⁾.

¹⁾ The maximum limit was given more correctly in the 1907 Edition as 0,980.

Juniper Oil (*Oleum Juniperi*). $d_{15,50}$ 0,862 to 0,890¹⁾; α_D usually about $- 4$ to $- 6^\circ$, rarely exceeding $- 12^\circ$. Oil from the leaves and branches has opt. rot. about $+ 8,5^\circ$.

¹⁾ We have found commercial oils of good quality to possess a sp. gr. of 0,860.

Lavender Oil (*Oleum Lavandulæ*). $d_{15,50}$ 0,882 to 0,900; ester content (linalyl acetate) 7 to 11% (English oil) and 25 to 45% (French oil)¹⁾.

¹⁾ In the case of steam-distilled oils as much as over 50% is observed.

Lemon Oil (*Oleum Limonis*). $\alpha_D + 58$ to $+ 65^\circ$, occasionally up to $+ 66^\circ$; the optical test for the first 10% of the distillate has been omitted. Terpene-free lemon oil¹⁾: $d_{15,50}$ 0,895 to 0,900; $\alpha_D - 5$ to $- 8^\circ$; citral content 40 to 50%.

¹⁾ It is impossible to lay down definite limits of value for terpene-free oils, as their properties vary according to the process of manufacture.

Lemongrass Oil¹⁾ (*Oleum Graminis citrati*). $d_{15,50}$ 0,895 to 0,905; in West Indian Oil 0,878 to 0,882²⁾; minimum citral content (bisulphite method) 70%.

¹⁾ *Andropogon citratus*, D. C. is mentioned as the parent-plant, a designation which, according to the most recent investigations, applies only to the variety of lemongrass which yields the imperfectly-soluble oil. Comp. Report April 1907, 33, 34.

²⁾ In this case also the sp. gr. is very frequently considerably higher.

Mustard Oil (*Oleum Sinapis volatile*). B. p. 147 to 156°.

Nutmeg Oil (*Oleum Myristicæ*). $d_{15,50}$ 0,870 to 0,930; $\alpha_D + 13$ to $+ 30^\circ$ ¹⁾; sol. in 3 vols. 90% alcohol.

¹⁾ Oils prepared in our own works from the best material have given opt. rot. as low as $+ 7^\circ 52'$. Comp. Report October 1904, 66.

Orange Oil (*Oleum Aurantii*). $d_{15,50}$ 0,847 to 0,854¹⁾; $\alpha_D + 95^\circ$ ($+ 92^\circ$ or 'bitter oil')²⁾ to $+ 98^\circ$.

¹⁾ In Bitter Orange Oil the sp. gr. ranges from 0,852 to 0,857; in sweet oil from 0,848 to 0,853.

²⁾ We have observed a minimum of 89° in bitter oil of unquestionably reliable origin.

Pennyroyal Oil (*Oleum Pulegii*). $\alpha_D + 13$ to $+ 35^\circ$.

Peppermint Oil (*Oleum Menthæ piperitæ*). $\alpha_D - 18$ to $- 35^\circ$, rectified oil is soluble in 4 vols. of alcohol (70%).

Pimento Oil (*Oleum Pimentæ*). $d_{15,50}$ 1,030 to 1,050¹), eugenol content 60 to 75%²).

¹) We have observed a minimum of 1,024 in oils distilled by ourselves.

²) We have observed up to 80% in our own distillates. The estimation must be carried out with 3% solution, as otherwise the results are too high.

Pine Oil (*Oleum Pini*). $d_{15,50}$ 0,865 to 0,870¹); α_D — 5 to — 10°.

¹) We have already pointed out on a previous occasion (Comp. Report October 1906, 62) that of recent years numerous oils of *Pinus Pumilio* are brought into commerce which show lower sp. gr. and a higher opt. rot. and yet are of exquisite quality. In judging the properties of an oil this fact should be taken into account.

Pine Oil, Siberian (*Oleum Pini Sibiricæ*). $d_{15,50}$ 0,900 to 0,920; α_D — 3 to — 42°; bornyl acetate content 30 to 40%.

Geranium Oil (*Oleum Geranii*). $d_{15,50}$ 0,890 to 0,906. Bourbon oil 0,885 to 0,895; ester content (geranyl tiglate) of the French oils 23 to 29%, of the Algerian oils 25 to 28% and of the Bourbon oils 30 to 35%¹.

¹) We have found Algerian oils to contain from 13 up to 29,5% and Bourbon oils from 21 up to 33% geranyl tiglate.

Rose Oil (*Oleum Rosæ*). $d_{15,50}^{30}$ 0,854 to 0,862¹); α_D — 2 to — 4°²; n_{D25} 1,460 to 1,465³); cong. pt. + 18 to + 22°, usually about 20°.

¹) The minimum limit given is too high; it should be 0,849.

²) We have found oils of good quality with opt. rot. down to — 1°. Comp. also p. 10 of the present Report.

³) The co-efficient of refraction of good Bulgarian oils, according to our experience, frequently lower; we have observed a minimum of 1,452.

Rosemary Oil (*Oleum Rosmarini*). $d_{15,50}$ 0,895 to 0,920; α_D usually dextrorotatory, + 1 to + 12°, English and Spanish oils are often slightly lævorotatory; sol. in 5 to 10 vols. 80% alcohol. Borneol content 10 to 16%, bornyl acetate content 2 to 5%. The estimation of the rotation of the initial 10% of the distillate is omitted.

Rue Oil (*Oleum Rutæ*). α_D + 0° 13' to + 2° 30' ¹).

¹) We have already pointed out on the occasion of our previous criticism that faintly lævorotatory rue oils are occasionally met with.

Sandalwood Oil, East Indian (*Oleum Santali*). $d_{15,50}$ 0,973 to 0,984; α_D — 13 to 21°. Santalol-content ($C_{15}H_{24}O$) not less than 90%, generally 92 to 98%.

Savin Oil (*Oleum Sabinæ*). The oil distilled from *Juniperus phœnice* has a lower sp. gr. ($d_{15,50}$ about 0,890) and a lower optical rotation (α_D + to + 5°) than has true savin oil¹).

¹) Comp. with regard to this Report April 1906, 61; October 1906, 72; April 1907, 93.

Spearmint Oil (*Oleum Menthæ viridis*). α_D — 36 to 50°.

Thyme Oil (*Oleum Thymi*). Phenol-content 20 to 45%, to be estimated with 5% solution; usually 3 parts of 70% alcohol are required to dissolve the oil, though sometimes 10 or more.

Turpentine Oil (*Oleum Terebinthinæ*). α_D of the American variety almost invariably dextrorotatory, $+1$ to $+15^\circ$, occasionally also slightly lævorotatory.

Turpentine Oil, Rectified (*Oleum Terebinthinæ rectificatum*). $d_{25}^{25^\circ}$ 0,860 to 0,865¹ (U. S. Ph.).

¹) The minimum limit of value relates to a temperature of 15° , for $\frac{25^\circ}{25^\circ}$ it is 0,853.

Wintergreen Oil, Natural.

a) *Oleum Betulæ* (from *Betula lenta*, L.). $d_{15,5^\circ}$ 1,179 to 1,187; sol. in 6 vols. 70% alcohol.

b) *Oleum Gaultheriæ* (from *Gaultheria procumbens*, L.). $d_{15,5^\circ}$ 1,180 to 1,187; sol. in 6 vols. 70% alcohol.

Wormseed Oil, American (*Oleum Chenopodii*). $d_{15,5^\circ}$ 0,970 to 0,990¹); α_D — 1 to — 6°.

¹) The minimum limit is too low. Comp. Report April 1908, 109.

Japanese Pharmacopœia.

The *Deutsche Japanpost* of January 20, 1912 (No. 43, p. 14), contains an article on additions to and alterations in the *Pharm. Japonica III*. Among the preparations there mentioned is sandalwood oil, which is thus referred to:

“*Oleum Santali* is a viscous, pale yellow or yellow, optically active liquid (α_{D20° — 16 to — 20°). Its b. p. lies between 275 and 280°, at 292 to 300° it loses over 70% in weight. When two drops of *Oleum Santali* are introduced into a mixture consisting of 9 cc. glacial acetic acid and 1 cc. hydrochloric acid, the solution should not acquire a red or violet colour within the lapse of 5 minutes.”

It is not clear from the article in question whether these data are already officially in force, or whether they relate to proposed alterations only, as the “additions and alterations” are published without any comment. Apart from the optical rotation, however, the amplifications cannot be described as a happy selection. It would have been better if no details had been given of the boiling point, or rather of the boiling temperature, especially in view of the fact that those mentioned above are not even correct. If the distillation is carried out in the proper manner, that is to say so that the entire mercury-column of the thermometer is surrounded by the vapour arising from the liquid, it will be found that only a very small portion of the oil (about 10%) passes over below 300°, which is quite natural, seeing that the b. p. of santalol, which forms over 90% of the bulk of the oil, lies above 300°. In any case the behaviour on boiling depends altogether upon the experimental conditions (shape and size of the flask, mode of fixing the thermometer, &c.) which explains,

among other things, why different investigators have in the past obtained different results¹⁾.

Another serious error lies in the incorporation of the colour-reaction which was recommended at the time by Conrady for testing sandalwood oil. We have repeatedly pointed out²⁾ that this reaction is quite useless for sandalwood oil evaluation.

Chemical Preparations and Drugs.

Aldehydes, Higher. It has been ascertained (chiefly in our laboratories), that the characteristic carriers of the odour of a large number of oils of the first practical importance in perfumery and in the manufacture of essences are a series of the so-called higher aldehydes. These aldehydes have been named after the number of carbon-atoms contained in them and among them the following have been found to occur in essential oils: octylaldehyde (with eight carbon-atoms, C_8) in lemon oil; nonylaldehyde, C_9 , in German rose oil, Ceylon cinnamon oil, mandarin oil, orris root oil, and probably also in lemon oil; decylaldehyde, C_{10} , in sweet orange oil, lemongrass oil, mandarin oil, orris root oil, neroli oil, cassie flower oil; duodecylaldehyde or laurinaldehyde, C_{12} , in pine needle oil from *Abies pectinata*.

Although these aldehydes occur only in fractions of one per cent they are of very material importance in determining the odour of the oil. They all possess a marked odour peculiar to themselves, and generally of a refreshing, fatty-sweet character, somewhat varying, of course, in each member of the series. The particular shade of odour peculiar to each separate aldehyde only becomes perceptible in high dilution, as, for instance, in alcoholic solution.

We have now incorporated into our lists a series of these higher aldehydes, namely octylaldehyde, nonylaldehyde, decylaldehyde, undecylaldehyde, and duodecylaldehyde (laurinaldehyde). The applicability of the aldehydes may be inferred in part from their occurrence in the natural oils, as stated above, that is to say, they can be used in the first place in the preparation of the corresponding synthetic oils, such as sweet orange oil (decylaldehyde), lemon oil (octyl- and nonylaldehyde), rose oil (nonylaldehyde) and so on. Further, according to recent experiments by leading French perfumers, some of the aldehydes in question will find a new field of usefulness in the preparation of fine perfumes. Duodecylaldehyde, in particular, when added to α -ionone in proportions of 5% or

¹⁾ Comp. Gildemeister and Hoffmann, *The Volatile Oils*, p. 340.

²⁾ Report October 1897, 54; April 1904, 82.

to β -ionone in proportions of 10%, is credited with imparting to violet-scent mixtures prepared with it their much-esteemed, refreshing, herb-like, so-called "green" aroma. A similar addition will serve to revive and thereby save such preparations as violet-extracts which, when made according to the usual recipes, have a flat and inexpressive odour. From another quarter the same aldehyde is recommended for scent of an orange-character, and also, in particular, to produce the effect of lily-of-the-valley.

It appears to us, however, that for oils of the *Citrus* species the lower aldehydes (decyl- or possibly undecylaldehyde) would be more suitable, especially for such scents as Eau-de-Cologne and others of that kind. Octylaldehyde is reported to be particularly adapted for scent mixtures of the character of "Jasmine rose", while nonylaldehyde, as already stated, is chiefly suitable for producing rose-like effects.

The aldehydes above referred to may perhaps be regarded as the most productive and subtle synthetic perfumes at present known. In accordance with these qualities they must be handled and stored with the greatest care. They are best kept in solutions of from 5 to 10% in the purest alcohol and in dark, fully-filled bottles in a cool place. When measuring out the quantity to be added, the perfumer must bear in mind that only very small proportions may be used, say about 0,1% for oils, a correspondingly larger proportion for terpeneless synthetic oils, and a correspondingly smaller one for extracts. As an over-dose is more likely to be harmful than an under-dose, the greatest care should be taken with the addition.

Undecyl- and duodecylaldehyde (laurinaldehyde) are only supplied by us in 10% alcoholic solution, because of their very limited keeping-power.

We must expressly point out that we are not in a position to give more precise directions for the use of our new aldehydes and we therefore earnestly advise those who have not thoroughly mastered the art of fine perfumery in all its branches, to abstain from experimenting with these costly preparations, which require for their successful use a thoroughly trained sense of smell and complete familiarity with all the aids of modern perfumery.

Benzyl Acetate, free from chlorine. In the course of the past half-year inferior qualities of this ester (which, to be sure, had the doubtful advantage of being low-priced) have repeatedly been submitted for our opinion. As already pointed out in our last Report (p. 111) a preparation, to be of good quality, must contain from 98 to 100% ester and must be free from chlorine-compounds. Neither condition was existent in the samples submitted to us, the ester-content falling as low as 91,5%.

Benzyl Benzoate. The recent examination of a sample of "cheap" benzyl benzoate proved once more that there is always a natural ex-

planation of such "cheap" prices. The sample submitted to us had the following characters: d_{150} 1,1198, n_{D200} 1,56836, ester-content 93,7%. Its inferior quality was revealed in the first place by the ester-content, which was much too low, the specific gravity and index of refraction being also below the mark. The product, furthermore, did not solidify below about 15,5°, whereas the solidifying point of a preparation which answers the requirements is about 18°. In determining the solidifying point it is necessary to cool down the oil to about +10°, as otherwise the process of solidification proceeds too slowly.

We desire to call attention to the necessity of always stipulating that benzyl benzoate, whatever the conditions, should have an ester-content of from 98 to 100%. The sp. gr. of a preparation of good quality lies between 1,121 and 1,125 and the index of refraction between 1,569 and 1,570 (20°).

Borneol. The *Revue scientifique* (1911, p. 82)¹⁾ contains an article on Borneo-camphor, which is here referred to in passing because we have on several occasions dealt with the principal subject-matter of the contribution, which is chiefly devoted to a description of the collection of the drug²⁾

Civet. We cannot too frequently direct attention to our excellent assorted stock. At the present time a somewhat large shipment is on the way for us, and judging by the samples to hand, its quality may fairly be described as exquisite. We hope that it may not be necessary to alter our selling-prices, but the article is very firm indeed, the demand for really good qualities being quite keen.

Menthol. Generally speaking, adulteration of menthol is seldom heard of in the wholesale trade, and for that reason a recent experience of ours in connection with the delivery of a parcel of menthol may be of interest. When the residual mother-liquor after the first recrystallisation of the crude product was about to be again worked up for menthol, we obtained crystals which, although similar to menthol in appearance, had a much higher melting-point and contained a considerable proportion of halogens. After repeated recrystallisation from dilute alcohol they finally gave m. p. 76°. Our surmise that these crystals consisted of α -bromo-camphor was confirmed both by the pronounced halogen-reaction and by the fact that, when reduced with zinc-dust and glacial acetic acid, they could be converted into camphor; the last-named body being identified from its oxime and its semicarbazone.

Whether the adulteration had been practised in Japan or in England, where the parcel had been in warehouse for some considerable time, could

¹⁾ Quoted from *Annal. de Pharm.* 17 (1911), 489.

²⁾ *Comp. Report* April 1905, 99; April 1907, 25; October 1910, 149; April 1911, 13.

not be discovered, but in any case we desire to call attention to a form of adulterant which will most probably again be found in menthol on several occasions, especially when menthol-prices are high.

We report on the market-position of menthol under peppermint oil, Japanese, p. 102.

Musk, Tonquin. For some considerable time the price-fluctuations of this important article have moved within a narrow compass. As may be imagined, the musk-trade in China has suffered severely during the last few months from the effects of the Revolution, and the supplies from the interior to Shanghai have been completely suspended. Nevertheless the market has not been affected in any way, and it may therefore be concluded that the stocks in the principal consuming countries were sufficient, and that this was the reason why the cessation of trade in the country of production has failed to make any impression.

Exports of musk from Shanghai in the year 1911.

Year	to Paris	to London	to New York	to Germany and Austria	Total
	Catties	Catties	Catties	Catties	Catties
1911	417	155	317	20	909
compared with					
1910	722	239	287	65	1313
1909	480	161	186	60	887
1908	666	37	211	9	923
1907	829	57	337	37	1260

Peru Balsam. In a critical review of the method for the determination of cinnamine in Peru balsam prescribed in the German Pharmacopœia Ed. V, F. Lehmann and A. Müller¹⁾ call attention to certain imperfections in the Pharmacopœia-prescription.

The first of these imperfections is that the volume of the cinnamine which has gone into solution is entirely disregarded in the calculation. If, as prescribed, 2,5 g. balsam is shaken up with 50 cc. ether and the necessary quantity of liquor, the ether layer, when the mixture has been left to settle, does not represent 50 cc., as is assumed in the Pharmacopœia-test, but 51 cc. This means that in following the Pharmacopœia-method over 1% cinnamine less is taken into account than is actually found present when the figures used represent the real conditions.

Stöcker²⁾ had already called attention to another cause of error. He had discovered that when the alkaline ethereal balsam mixture is not shaken

¹⁾ Arch. der Pharm. 250 (1912), 1.

²⁾ Apotheker Ztg. 26 (1911), 283.

sufficiently long the cinnamine-values are too low. This is confirmed by Lehmann and Müller, who have found that the best method of correcting this error is not to add the liquor until the balsam alone has been shaken with ether for some time.

The addition of tragacanth as a clarifier is much to be recommended but a smaller quantity than that stated by Fromme (Annual Report of the firm of Cæsar & Loretz, Halle a. S., 1909) will suffice. This agrees with our experience.

Lehmann and Müller regard it as preferable to carry out the entire cinnamine-determination volumetrically, and for this purpose they give the following prescription:—

To 2,5 g. Peru balsam add 5 g. water, shake, add a weighed quantity of 30 g. ether and shake the mixture for one minute. Add 5 g. soda liquor again shake for 1 minute, leave standing for about 10 minutes and then carefully pour off the layer of water until only about 3 cc. is left. Next add 0,5 tragacanth and shake vigorously. After from 3 to 5 minutes, pour the principal quantity of the ether-solution (25 to 28 g.) into a wide-necked small flask, which, together with the cover, has been carefully tared, and determine the weight of the ether-solution. When the ether has evaporated in the water-bath the viscous cinnamine residue is dried for from 30 to 45 minutes at about 100°, allowed to cool in the desiccator and weighed.

If, with 2,5 g. Peru balsam and 30 g. ether, the quantity of ether-cinnamine solution used up in the experiment equals a grams, and if after evaporation of the ether, these are found to have yielded b grams cinnamine, the percentage of cinnamine-content in the Peru balsam is ascertainable by the following formula:—

$$\frac{1200 \cdot b}{a - b}$$

We may further state, although the fact is self-evident, that when a cinnamine-estimation is carried out according to the German Pharmacopœia, Ed. V, care should be taken that the temperature throughout the experiment is as equal as possible, as the volume of the ether-layer is subject to fairly considerable changes as a result of alterations in temperature.

Pollantin. As stated in our last Report (p. 114), our new Pollantin salve has been favourably received by the great majority of patients to whom we have sent samples with a request to give the article a trial. According to medical reports the percentage of patients whose condition was considerably ameliorated by the use of this ointment was 53, that of patients showing a partial improvement 32, and that of patients who failed to obtain relief from the remedy 15. The new preparation, which is supplied in the same manner as are our other Pollantin-preparations, has been

placed upon the market in the hope that it will bring relief to many hay-fever patients who, in spite of all precautions, were unable to obtain really good results from the previously available Pollantin-preparations.

After prolonged experiments Prof. Dunbar has been successful in discovering an effective mode of administering Pollantin as a remedy in the exceedingly troublesome form of asthma which afflicts certain patients in the later stages of hay-fever. His process consists in compressing the finest sifted Pollantin-powder, together with sugar of milk and a suitable binding-material, in the form of tablets, which are slowly dissolved in the mouth. Numerous patients to whom we have sent samples of the the remedy for trial report that the tablets have afforded them the desired relief, but before we place the preparation upon the market we desire to collect further opinions, and we shall be pleased to place experimental samples at the disposal of the medical profession, and to receive reports on their therapeutic action.

We desire once more to inform our customers, and in particular the pharmacists among them, that we are prepared to receive old tins of *liquid* Pollantin bearing control numbers below 153 in exchange for fresh serum, and we therefore request them to look out such numbers, if any, from their stocks, and to send them to our Branch Office. Upon receipt the new tins will be forwarded by return. In reply to numerous enquiries we may add that, as *powdered* Pollantin has unlimited keeping quality, it cannot be exchanged.

Rose "Schimmel & Co." (Red Rose). The success of this speciality exceeds our highest expectations. We are able to say without exaggeration that no novelty of the past decade has been received by the manufacturing perfumery-trade with anything like the acclamation which has been bestowed upon this article: our sales-book is the best witness of this assertion. The extension of our rose-plantations which has been carried out last autumn was mainly determined by our growing requirements of the natural rose-extract, which, as is well-known, forms the basis of the preparation, and to which the manufactured article is chiefly indebted for its excellence. It is to be hoped that last year's crop-failure will be followed, this season, by a normal output, so that we may be in a position to prepare enough to meet the demand.

Safrol. When, in the course of last summer, the large supplies of camphor oil received by us had been for the greater part used up, we were able to reduce the price of safrol somewhat. After this we concluded most important contracts for delivery, which shows once more that our manufacturing capacity is planned on a scale which enables us to meet all competition at home or abroad. As always, the United States has been the principal consumer, considerable quantities of safrol finding a market in that country for all manner of purposes. In view of the general

condition of the artificial perfume industry we regard it as improbable that there will be any need for reducing the price to a material extent within the next few months.

Thymol. The trade in this article has been unable to recover from the senseless competition which has ruined it. Since our last Report the prices of ajowan-seed have become somewhat firmer, but in spite of this it is impossible to bring about a corresponding rise in the quotations for thymol, because some of the principal producers, calculating the price of the manufactured article on the basis of the cheap raw material prevailing some time ago, are determined to underbid. It is fortunate that our branch of industry offers no other similar example of mutual "freezing-out", and it must be a matter for surprise that the Hamburg manufacturers, who are the parties most concerned, have not yet grown tired of continuing this preposterous competitive fight. Speaking for ourselves, we have no difficulty in disposing of our make at our own prices.

Notes on Scientific Research in the Domain of the Essential Oils.

General.

In a treatise by Alice Henkel¹⁾ on American medicinal plants we find some data on the habitat of numerous plants which are used in the manufacture of essential oils. Wintergreen (*Gaultheria procumbens*, L.) occurs on sandy spots in cool, damp woods, and especially underneath evergreen trees in Canada and the North-Eastern States of the Union. Catnip (*Nepeta Cataria*, L.) which was imported from Europe, now grows throughout North America, from Canada and Minnesota in the North to Virginia and Arkansas in the South. The geographical distribution of pennyroyal extends from Nova Scotia and Quebec in the North to Dakota in the South. Bugleweed (*Lycopus virginicus*, L.) is found from Canada to Florida, Missouri and Nebraska. Peppermint (*Mentha piperita*, L.), an importation from Europe, occurs from Nova Scotia and Minnesota in the North to Florida and Tennessee in the South. The boundaries of the geographical distribution of spearmint (*Mentha viridis*, L.) a plant which has also been brought over from Europe, are Nova Scotia, Utah and Florida. Canada Fleabane (*Erigeron canadensis*, L.) inhabits the greater part of North America. The Yarrow (*Achillea Millefolium*, L.) extends from New England to Missouri. Tansy (*Tanacetum vulgare*, L.) has been carried over from Europe to America and is now found from New England and Minnesota as far as North Carolina and Missouri, Wormwood (*Artemisia Absinthium*, L.) is also a native of Europe; it inhabits the North Western part of the United States from Newfoundland to New York. Fireweed (*Erechtithis hieracifolia*, Raf.) has a geographical distribution extending from Canada to Louisiana and Nebraska.

On p. 147 of our Report of April 1911 we referred to the experiments in the cultivation of medicinal plants which are being carried on in Austria by W. Mitlacher. Further information on this subject is given in a reprint from the *Zeitschrift f. d. landwirtschaftliche Versuchswesen in Österreich*, 1911, of which a copy has been kindly sent to us by the author.

Sachsse & Co.²⁾ have investigated the influence of peroxide of hydrogen upon agents for correcting the taste of mouth-washes. They admixed 0.05 g. of the essential oil under examination to a mixture of 40 g. alcohol (90% by vol.), 30 g. water and 25 g. peroxide of hydrogen (12%). After standing for one to two months the taste of this mixture was compared with that

¹⁾ U. S. Department of Agriculture, Bureau of Plant Industry, Bull. No. 219.

²⁾ Apotheker Ztg. 27 (1912), 19.

of a precisely similar freshly-prepared mixture. It was found that peroxidation of hydrogen causes a pronounced alteration in geraniol, menthol, menthyl acetate, peppermint oil, and cinnamic aldehyde; that it effects a less pronounced change in carvacrol, eugenol, geranium oils, clove oil and terpineol and that it leaves unaffected anethol, Russian anise oil, bornyl acetate, eucalyptus oil, Siberian pine-needle oil, star anise oil, and thymol.

Bibliography.

Those who desire to acquire a knowledge of the nature of refraction as well as of the coefficient of refraction (the latter being an important factor in the examination of the separate constituents of essential oils) will find in the *Refraktometrisches Hilfsbuch* lately published by Veit & Co. Leipzig (1911), an excellent guide. In the introduction to the work, the authors, Prof. Dr. W. A. Roth and Dr. F. Eisenlohr, who are known by their researches in the domain of the determination of chemical constitution by physical means¹⁾ explain the meaning of the terms "coefficient of refraction" and "molecular refraction", after which they deal with dispersion and its cause. In the following chapters they treat of the principles of refractometry and describe in detail the various refractometers. An important section of the book consists of chapters on the development of molecular refraction and dispersion as well as on exaltation and specific exaltation. Want of space forbids us from entering into details on the abundance of interesting material in the book, but we cannot omit to mention that it contains an exact guide to the determination of specific gravity by means of various pycnometers and at different temperatures as well as many tables, including logarithm-tables up to the fifth decimal which greatly facilitate calculations.

Analytical Notes.

The passage in our Report of October 1911 (p. 119) relating to J. Herzog's suggestions on the subject of the test for chlorine compounds in benzaldehyde has caused that author to make a reply²⁾ in which he again lays stress upon the advantages of the modification proposed by him, and in which he leaves it to his fellow-chemists whether they will adopt his method or ours.

G. Heyl³⁾ and E. Rupp⁴⁾ have also intervened in the discussion on this subject. Heyl recommends the lime-test for chlorine, which he carries out as follows: —

¹⁾ Comp. Report October 1910, 164, 167; October 1911, 122.

²⁾ Berichte d. deutsch. pharm. Ges. 21 (1911), 536.

³⁾ Apotheker Ztg. 27 (1912), 49.

⁴⁾ *Ibidem* 92.

1 to 2 gr. chlorine-free hydrate of lime are stirred up with a glass rod in a small porcelain dish with 10 to 15 drops benzaldehyde, the mixture is then covered with a thin layer of hydrate of lime and slowly brought to a red heat. After cooling the contents of the dish are poured into a beaker, 5 to 6 cc. water are carefully added, and the mixture is faintly acidulated with nitric acid. The solution is then filtered through chlorine-free filtering paper or glass-wool and is tested for chlorine with silver nitrate.

By this method Heyl was able to trace clearly so small a proportion of chlorine as 1 drop of monochloro-benzene in 50 gr. benzaldehyde.

Rupp proposes for the same purpose the copper oxide test (the so-called Beilstein test) for which he gives the following *modus operandi*:—

A copper wire, or, better still, a strip of copper wire-netting 0,5 cm. in width (about 1 mm. mesh) is twisted at one end into a narrow spiral shape, forming a roll about the diameter of a large pea. This roll is repeatedly drawn through a non-luminous flame in order to oxidise the surface of the copper and to remove any yellow or green coloration. When cooled, the roll is dipped into the benzaldehyde under examination and is then exposed to the flame for a moment in order to inflame the benzaldehyde. When the benzaldehyde is burnt off (not in the flame) the roll is again applied to the top of the flame. If there is a green inflammation, chlorine is present.

A roll of netting absorbs about 0,3 gr. and a wire-spiral about 0,1 gr. of the substance to be tested. Rupp found that when a roll of wire netting was used, so small a mixture as 1 drop benzylchloride in 50 gr. benzaldehyde gave a clearly perceptible reaction, whereas with copper-wire a mixture of 50 gr. benzaldehyde and 2 drops of benzylchloride was needed to produce such a reaction.

We ourselves have also suggested both these methods for the detection of chlorine in essential oils and preparations¹⁾, but notwithstanding this we prefer the combustion method for the purpose here under discussion, that method having been specially worked out for the testing of bitter almond oil for chlorine. Our experience shows it to be superior to the lime-test (although in itself that test is a sensitive one), inasmuch as it can be carried out more rapidly, especially when a series of oils is to be tested. And where minute proportions of chlorine are concerned, the copper test is decidedly inferior to both the combustion and the lime-methods, not only in respect of sensitiveness, but especially in respect of certainty of action. Hence the copper test can only be recommended under reserve and for the purposes of a preliminary examination.

¹⁾ Gildemeister and Hoffmann, *Die ätherischen Öle*, 2nd Ed., Vol. I, p. 630.

In our last Report (p. 121) we mentioned a paper by Fuller¹⁾, in which he recommended Walther's hydroxylamine method (Report April 1900, 2) for estimating the camphor-content of spirits of camphor. E. K. Nelson has now investigated the general applicability of this method to ketones and has found it to give tolerably satisfactory results with carvone, pulegone, camphor, thujone, and menthone. He therefore regards it as suitable for the quantitative estimation of the ketones in question, especially in cases where these ketones constitute the principal portion of an oil. But in the case of oils in which the ketones occur only as constituents of secondary importance it is necessary to make further special investigations to determine how the other constituents behave when attacked by the reagent.

Several determinations made by Nelson with various oils have given the following results:—

Spearmint oil	58,4	or	53,1%	carvone
" "	65,5	"	66,4%	"
" "	61,4	"	60,7%	"
Tansy oil	68,6	"	65,4%	thujone
Wormwood oil	33,2	"	31,2%	"
Pennyroyal oil	81,9	"	— %	pulegone
Rosemary oil	30,3	"	30,2%	camphor

Experiments made by Nelson with fenchone showed the quantitative estimation of that body to be impossible by Walther's method.

Judging from our own present experience with this method our attitude towards Nelson's optimistic views is somewhat sceptical, but we are not prepared to express a definite view on the matter. In commenting upon Fuller's article at the time (Report October 1911, 121) we stated that a control-test made by us for determining the camphor-content of spirits of camphor had failed to give satisfactory results.

In our October Report of 1910, p. 139, we mentioned the method for testing turpentine oil which has been worked out by Louise, and which is based upon the miscibility of this oil with aniline, and the determination of the so-called curve of miscibility. The same author³⁾ has recently applied the same principle to the examination of lavender oil, neroli oil, lemon oil, peppermint oil, sandalwood oil and copaiba balsam oil. It would appear that by plotting a miscibility-curve it is possible to discover adulteration in oils of lavender and neroli and to differentiate between French Japanese and American peppermint oils.

¹⁾ Published also as Circular No. 77 of the Bureau of Chemistry, U. S. Dept. of Agriculture.

²⁾ U. S. Dep. of Agriculture, Bureau of Chemistry. Bulletin No. 137 (20. VII. 1911), p. 186.

³⁾ Journ. de Pharm. et Chim. VII. 4 (1911), 194.

Methods for the determination of citral in lemon oil are described on p. 75.

On the determination of the number of ethylene linkings in hydroaromatic bodies, see Chemical Notes, p. 165.

Physical Notes.

We have before us for comment several interesting papers by A. Golodetz.

1. "On new methods for the separation of mixtures with closely-approximating boiling-points, and of mixtures which boil without decomposition"¹⁾. For the purpose of separating mixtures of liquids the author availed himself of the property of many mixtures of distilling at a temperature lower than the boiling-temperature of the pure components of the mixture. To a binary solution distilled at minimum boiling-point, which therefore cannot be completely separated by fractional distillation, Golodetz adds a third body which also boils at minimum boiling-point with one of the components of the mixture, and at a temperature which must be lower than that of the binary mixture.

Toluene, for example, boils at $110,4^{\circ}$, acetic acid at 118° . Now, if a mixture in any proportion of these two liquids is distilled, there passes over at 104° a distillate which is always composed of $31,9\%$ by weight of acetic acid and $68,1\%$ toluene, and upon increasing the distilling-temperature there distils over the liquid which was present in excess of the mixture-proportion mentioned above. Separation by fractional distillation is therefore impossible by this method. It can be accomplished, nevertheless, when to the mixture a third body is added which distils over at minimum boiling point with one of the two other components of the mixture; that is to say, with the acetic acid if it is desired to keep back the pure toluene in the evaporation, or with the toluene if it is desired to keep back and gain the pure acetic acid. Such bodies are, in the first place benzene, in the second, water.

The author now made the following experiment: he mixed 68,1 g. toluene with 31,9 g. acetic acid and, in order to be able to distil off the acetic acid in the receiver, and to obtain the toluene in the pure form, added a quantity of benzene corresponding to the composition of the steam when benzene and acetic acid distil over together at minimum boiling-point. In the present case this quantity was rather large (1800 g.), for at minimum boiling point the mixture only contains 2% acetic acid and 98% benzene. Golodetz distilled the entire mixture in a still with a fractionating-head and obtained in the last fraction 46,1 g. pure toluene, or $67,5\%$ of the total quantity employed.

¹⁾ Journ. russ. phys. chem. Ges. 43 (1911), 1041. Quoted from Chem. Zentralbl. 1912, I, 68.

The following experiments in separation were carried out in a similar manner: —

To a mixture of 127 g. acetic acid and 274,4 g. toluene Golodetz added 67 g. water (minimum boiling point of the mixture of water and toluene 81,4°, proportion 19,6% water). Fractional distillation gave for the highest boiling fraction 64 g. pure acetic acid = 50,2% of the quantity present in the mixture.

242 g. toluene mixed with 60 g. benzene were diluted with 39,5 g. methyl alcohol (b. p. 64,7°) (minimum boiling point of the mixture of methyl alcohol and benzene 58,35°; proportion 60,45% benzene). After fractional distillation 228,5 g. pure toluene was obtained.

Also:

36,3 g. benzene, b. p. 80°	} minimum b. p. of the mixture 58,35°
23,7 g. methyl alcohol, b. p. 64,7°	
170 g. carbon disulphide, b. p. 46°	} minimum b. p. of the mixture 38,3°
	} proportion methyl alcohol 12—13%

Result: 23 g. pure benzene = 63,4%.

Also:

45 g. ethyl butyrate, b. p. 119,9°	} minimum b. p. of the mixture 94,2°
15 g. amyl bromide, b. p. 118,5 to 119°	
39 g. <i>n</i> -propyl alcohol, b. p. 97,2°	
Result: 30 g. ethyl butyrate = 66,7%.	} proportion propyl alcohol 70,7%.

The experiments mentioned by the author are only intended to explain the method; it is not claimed that they are all of practical usefulness.

The method of separation by distilling, making use of the minimum b. p. was known¹⁾. But to Golodetz belongs the merit of having again illustrated by striking examples this property of numerous mixtures which is so little used in practice.

At the conclusion of his paper the author states "from all the above experiments it is evident that the mixtures which boil without decomposition behave like uniform chemical entities; a fact which has already been pointed out by Makowiecki."

The fact that a distilled solution possesses a constant temperature and a constant composition of steam does not of itself warrant the conclusion that it represents a chemical compound. It is only when the boiling point is also a maximum boiling-point that the presence of a molecular chemical compound may be assumed with certainty. The only exception to this rule which is at present known is a solution of formic acid in water which, although the melting-point curve shows a maximum b. p.

¹⁾ v. Rechenberg, *Gewinnung und Trennung der ätherischen Öle durch Destillation. Grundzüge einer allgemeinen Destillationslehre.* 1910. p. 593.

nevertheless forms no compound. But an additive compound which has a lower b. p. and at the same time a higher steam-pressure than its components is scarcely imaginable, and as a matter of fact has not yet been discovered. Probably the true explanation of the homogenous mixtures with minimum boiling point is to be found rather in conceiving them as transition-members between the heterogenous mixtures and the solutions proper. From an optical standpoint it is true that they are solutions, but for the rest their minimum boiling-point connects them more nearly with the mixtures of mutually insoluble or sparingly soluble substances.

2. "On fractional distillation in the laboratory and on new rectifying apparatus" ¹⁾. A. Golodetz here deals with the course of the process of fractional distillation of mixtures and with the conditions which should govern the construction of distilling-apparatus for laboratory use. He begins by explaining the familiar forms of such apparatus and then proceeds to explain a new model of fractionating-head, which he calls the "birectifier". We reproduce below the result of a trial distillation with this apparatus. The charge consisted of equal parts of benzene and toluene, and the steam-pressure was 746,5 mm.

Temp.-Interval	Quantity of Distillate
79,42 to 79,6 °	42 %
79,6 „ 80,4 °	3,95 %
80,4 „ 81,4 °	1,7 %
81,4 „ 83,4 °	0,8 %
83,4 „ 86,4 °	0,45 %
86,4 „ 89,4 °	0,35 %
89,4 „ 95,0 °	0,43 %
95,0 „ 100,5 °	0,72 %
100,5 „ 103,5 °	0,95 %
103,5 „ 106,5 °	0,98 %
106,5 „ 108,5 °	2,85 %
108,5 „ 109,3 °	4,25 %
Toluene (from the difference) 40,85 %	

The first and the last fraction might be regarded respectively as almost pure benzene and toluene.

For purposes of comparison the author has distilled quantities of 500 g. each of a single sample of turpentine oil in his own and in six other distilling-heads. In the details of these experiments no mention is made of the pressure, and whether in all the experiments it was precisely, and not only approximately the same. The action of a fractionating apparatus depends in the first place upon the pressure.

¹⁾ Chem. Industrie 35 (1911), 102 and 141.

3. "On new methods for the separation of mixtures of liquids of which the boiling-points are the same, or lie close together¹⁾." This paper is the first of a series of articles which apparently treats the subjects just referred to in greater detail. We intend to deal with this matter when the series is completed.

4. "On fractional distillation with steam²⁾." A. Golodetz has carried out several distilling-experiments with the object of discovering whether it is easier to separate a mixture of liquids with different degrees of volatility by means of distillation with water or by dry distillation. He obtained the following results: —

- "a) Fractional distillation of mixtures of substances insoluble in water and water (provided the b. p. be not too high), gives excellent results much better than those obtained by ordinary distillation under similar conditions.
- b) The distillation of mixtures of high b. p. gives less satisfactory results but when high rectifying apparatus is employed, distillation with water also answers very well in this case.
- c) In the course of the rectification-process the mixture distilled with water undergoes certain changes consisting in the simultaneous alteration of temperature and pressure, which changes proceed in different directions.
- d) The process of distillation is completely governed by Young's law according to which the quantity of liquid which has been distilled off in the presence of water up to the mean of the difference in temperature between the boiling-points of each component part, equal in quantity the whole of the first component, plus the corresponding quantity of water.
- e) The result of the fractionation depends upon the difference between the boiling points of the individual components with water, and upon the quality of the rectifying apparatus."

Apart from conclusions *b* and *d*, the other statements are incorrect. The author has made too light of his task. He makes two experiments in fractionation with a mixture of benzene-toluene and water, and then compares the results of this distillation with water with the results of a experiment in dry distillation made by another author. The separation in the said author's experiment having given less favourable results than in his own, Golodetz concludes that fractionation of the oil-mixture with water is the better method. In arriving at this conclusion, he happened to have hit upon a rather poor experiment in separation among those recorded in literature. Thus, for example, Young's distilling-experiments:

¹⁾ Chem. Ztg. 36 (1912), 273, 297.

²⁾ Zeitschr. f. physik. Chem. 78 (1912), 641.

³⁾ *Fractional Distillation*, London 1903, p. 174.

have given better results for fractionation without the aid of water as an evaporating-agent. Golodetz should have made the comparative test himself, using the same fractionating-head, and with the same rate of speed in distilling, and the same distilling temperature. For the separation of a mixture of vapours also depends, among other things, upon the extent of the partial condensation in the fractionating-head. In the well-known forms of fractionating-heads, as used in laboratory-work, and also in his own "birectificator", there takes place a process known as "wild dephlegmation", *i. e.* a process of condensing induced by the cooler outer air which defies regulation, and, this being so, the degree of steam-temperature, given equal heating, is also a factor in determining the measure of separation.

The other distilling-experiments of Golodetz also fail to bear out his assertion that fractional distillation with water yields better results than does ordinary distillation. He distilled a mixture of amyl formiate and amyl acetate with water, and obtained an excellent separation-effect, but he has not made any comparative distilling-experiment without water.

On p. 641 of his treatise the author states that fractional distillation by steam is quite a recent practice in essential oil chemistry. This assertion would be correct if he had added the words "in the public laboratories", for this mode of fractionation has been in use in the essential oil industry for the past half century or so.

In the course of our numerous comparative experiments, some of which have been published¹⁾, we have found that where the separation of homogenous mixture of liquids is concerned, distillation by water is less effective than dry distillation in cases where the mixture is not at all or only slightly soluble in water. But where one of the components of the mixture is soluble in water, that component is impeded, in water-distillation, in proportion to its degree of solubility in the evolution of steam. The component being thus kept back during the process, water-distillation in this particular instance gives an excellent fractionation, in particular when carried out with a fractionating-head.

In the process of water-distillation of mixtures of liquids which are not soluble in water to any extent, the steam only participates in the formation of vapour to this extent that, while it is passing through, an oil-free space is created into which the oil-mixture immediately commences to pour its vapour, until saturation-point has been reached. The steam determines the extent of the generation of vapour from the oil-mixture, but it does not influence the percentage of the oil-vapour. This is precisely the same as that of the saturated oil-vapour which rises from the same oil-mixture at the same temperature when no water is present.

¹⁾ v. Rechenberg, *Theorie der Gewinnung und Trennung der ätherischen Öle durch Destillation. Grundzüge einer allgemeinen Destillationslehre.* 1910, p. 383.

It may be said that steam, just as air or other indifferent gases, which is used as an evaporating-agent, plays the part of an air-pump.

In theory, therefore, water-distillation should be able to separate a mixture of liquids insoluble in water just as readily as is done by distillation without water at the same steam-temperature. But in practice it is found, *ceteris paribus*, that the separation-effect obtained with water-distillation is not so good, because when a fractionating head (or, working on a large scale, a column) is used, the exchange of the vapour mixture with the condensate (which is the determining factor when fractionating the oil-vapour), is disturbed and impeded by the quantities of water which are admixed with the oil and which in some cases overlay it. This is the reason why low-boiling mixtures of liquids are more readily separated by water-distillation than are less volatile mixtures: a fact which has also been observed by Golodetz. For in the case of the first-named mixtures the condensed steam contains comparatively little water, but in the case of the latter it contains a great deal. For example, 1 kilo steam when boiling takes place at atmospheric pressure, is capable of evaporating 9,11 kilos benzene or 5,82 kilos toluene, but only 0,18 kilos nitrobenzene or 0,05 kilos naphthalene.

Our Report of October 1910 contained a paragraph (p. 167) relating to a paper by Auwers and Roth on the thermic value of various terpenoid bodies. Soon after the publication of this paper the authors' attention was drawn to a slight experimental error, owing to which the ascertained values had been slightly below the actual. Auwers, Roth and Eisenlohr, however, have found that the theoretical conclusions which they had drawn from their previous experiments are in no way affected by the increase of the separate values.

A paper by Auwers and Moosbrugger²⁾ on the refraction and dispersion of organic substances³⁾ with several double linkings contains data concerning the dispersion and refraction-values of a series of alicyclic dienes⁴⁾ and other oxygenated compounds of an analogous constitution. The commonly accepted theory that all these compounds are spectrally chemically normal is in essence based upon conclusions of analogy which rest upon a very weak experimental foundation.

Examined spectrochemically the bodies under review showed no tendency towards exaltation either in their index of refraction or of dispersion.

¹⁾ Liebigs Annalen 385 (1911), 102.

²⁾ Liebigs Annalen 387 (1912), 167.

³⁾ Comp. Report October 1911, 122.

⁴⁾ Diènes, according to the Geneva nomenclature, are hydrocarbons with 2 double bonds.

A study of the data observed by the authors shows that neither the boiling point nor the density of an alicyclic diene affords any guide as to whether the body is one with conjugated or with isolated double linkings. Determination of the refractive index also is of little value. But by calculating the molecular refraction or dispersion, and by applying the values thus obtained in the testing of the preparations, much better results are afforded. Compensation of antagonistically active influences could only occur in cases where an acyclic diene without conjugation contained at the same time admixtures of a diene with conjugated double linkings and of a cyclic isomeric diene.

In order to prepare pure acyclic dienes, Auwers and Moosbrugger heated the unsaturated carbinols with bisulphate of potassium, a manipulation in which it is essential to remove the hydrocarbon which is generated as quickly as possible from the reaction-mixture. To achieve this object the best plan is to heat the alcohol and the sulphate under diminished pressure, while simultaneously passing dry hydrogen through the mixture.

Among other bodies, the authors have spectrochemically examined geraniolene (from geranic acid and from dimethyl heptenol), 2,6-dimethyloctene-2-ol-6 (from methylheptenone and magnesium ethyl iodide¹⁾, α - and β -cyclogeraniolene and homolinalool (2,6-dimethyl nonadiene-2,8-ol-6).

Auwers has also, in collaboration with Ph. Ellinger²⁾, investigated the problem of differentiating between hydroaromatic bodies with endocyclic and with semicyclic double linkings. Wallach's discovery that a semicyclic double linking regularly increases the molecular refraction above the normal value was of special importance in the identification of menthene derivatives. It also appeared to be desirable to ascertain the normal value of the specific exaltation which occurs in menthene hydrocarbons and to compare it with the exaltation values of the several varieties of conjugated systems.

The authors have re-calculated the observation-material collected by Wallach, using the densities compared with water at 4°, as well as the exact molecular weights and the atomic refractions determined by Eisenlohr³⁾. Generally speaking, the values for $E_{\Sigma D}$ deviated in only a few cases by more than + 0,1 from the ascertained mean; hence there was no occasion for determining the refractive index of other methene hydrocarbons, but it was necessary to discover whether these bodies also possessed an increased power of dispersion.

As was to be expected, the endocyclically saturated compounds not only exhibit a normal refraction, but also a normal dispersion and the moderate rise of the co-efficient of refraction in bodies with a semi-

¹⁾ See p. 177.

²⁾ Liebigs Annalen **387** (1912), 200.

³⁾ Comp. Report April **1911**, 155.

cyclic double linking corresponds with a clearly perceptible exaltation in the power of dispersion. The latter, however, is small and almost lies within the limits of error.

It is therefore possible to distinguish with clearness by the spectrochemical method between alkylcyclohexenes and alkylidene cyclohexanes.

In chemical literature a whole series of hydrocarbons is erroneously described as alkylidene cyclohexane derivatives, which in reality consists of endocyclically unsaturated compounds. Among these bodies, for example, are several hydrocarbons prepared by Sabatier and Mailhe¹⁾.

Finally, Auwers and Ellinger have investigated the cyclohexenyl acetic acids and the isomeric cyclohexylidene acetic acids, and in particular the esters of these bodies, with the result that they have found that in them there is a marked difference between the compounds with semicyclic double linking and the endocyclic non-saturated isomerides. The latter are in every respect normal, but the former display pronounced exaltation in their coefficient of refraction, and still more pronounced exaltation in their power of dispersion. The reason of this is obvious, inasmuch as the cyclohexylidene acetic acids not only possess a semicyclic double linking but also a conjugation, and the first effect of the latter is a powerful rise in refraction and dispersion.

As many of the free acids with semicyclic double linking have high melting points it is advisable to use the esters for optical examinations.

Hantzsch²⁾ calls attention to another physical property, namely absorption of the ultra-violet rays, which is of great importance in testing the purity of terpenes. Hantzsch has examined α -pinene, *d*-, *l*-³⁾ and *i*-limonene, dipentene, *l*- α -phellandrene, β -phellandrene, sylvestrene, caryophyllene, *m*- and *p*-cymene, *d*- and *l*-camphor, and *d*- and *l*-borneol. All these bodies (of which the experimental material had been placed by us at the disposal of the author), were purified by Hantzsch by fractionation, using a glass-bead column, in a Claisen flask in a current of carbonic acid gas at 10 to 15 mm., from a bath of Wood's metal. The solutions required for the determination of the ultra-violet absorption were prepared with optically pure ethyl alcohol; in order to obviate oxidation it is necessary to pipette the freshly-prepared distillates in measuring-flasks which have previously been filled with carbonic acid. Hantzsch does not give the constants of the bodies examined by him, which is to be regretted, because they would have made it possible to ascertain in how far the properties of the preparations in question are influenced by impurities. In the examination of terpenes distilled *in vacuo* it soon became evident that the absorption-method is much more sensitive than the refraction-method,

¹⁾ Compt. rend. 139 (1904), 343.

²⁾ Berl. Berichte 45 (1912), 553.

³⁾ In his paper, Hantzsch erroneously speaks of *l*-limonene as being prepared from orange oil. As a matter of fact, this terpene occurs in pine-needle oil.

inasmuch as such slight differences in the distilling-temperature as $\frac{1}{10}^{\circ}$ were perceptible in the shape and position of the absorption-curve. The curves of the preparations under examination have been plotted by Hantzsch in several tables, in which on the vertical lines he gives the logarithms of the layers in mm., corresponding to $\frac{1}{1000}$ normal solutions, and on the horizontal line the oscillation-figures in the ultra-violet rays. The absorption increases in proportion to the nearness of the double-linkings. It is weakest in pinene with the bridge-linking and in limonene with the greatest distance of two double-linkings; it increases in strength as the double-linkings draw nearer together (as in sylvestrene), and it reaches its maximum in the conjugated linkings, conjugation outside the ring (β -phellandrene) being more active than that within the ring (α -phellandrene).

A paper by J. F. Eijkman¹⁾ on the refractometric behaviour of a series of organic bodies contains particulars of the refraction and density of certain terpene-bodies: —

	Formula	t	d	n_{α}
Pulegane	C_9H_{18}	15,2	0,7799	1,42744
Pinic acid	$C_9H_{14}O_4$	109,4	1,0925	1,44581
<i>l</i> -Pinonic acid	$C_{10}H_{18}O_3$	110,7	1,0257	1,44621
α -Pinonic acid	$C_{10}H_{16}O_3$	109,1	0,9975	1,43812
α -Thujaketonic acid . . .	$C_{10}H_{18}O_3$	79,6	1,0115	1,44747
Pulegenic acid	$C_{10}H_{16}O_2$	17,5	1,0035	1,47989
Pulegamic acid	$C_{10}H_{18}O_2$	20,2	0,9618	1,45201
Ethyl puleganate	$C_{12}H_{22}O_2$	11,8	0,9178	1,44047
Pulegamic nitrile	$C_{10}H_{17}N$	16,2	0,8814	1,44751
Pulegano lactone	$C_{10}H_{16}O_2$	21,0	1,0146	1,46048
$\Delta^{4(8)}$ -Menthenol-1	$C_{10}H_{18}O$	80,0	0,8948	1,46277
$\Delta^{8(9)}$ -Menthenol-1	$C_{10}H_{18}O$	79,8	0,8703	1,44612
Fenchone	$C_{10}H_{16}O$	14,5	0,9488	1,46232
α -Fencholenic amide . . .	$C_{10}H_{17}ON$	117,9	0,9331	1,46216
β -Fencholenic acid	$C_{10}H_{16}O_2$	76,1	0,9638	1,45861
β -Fencholic acid amide . .	$C_{10}H_{19}ON$	108,2	0,9072	1,44683
β -Fencholic acid	$C_{10}H_{18}O_2$	18,9	0,9698	1,45469

G. Ciamician and P. Silber²⁾, in their twelfth paper on the chemical action of light³⁾, describe the effect of light upon toluene, *p*-, *m*-, and *o*-xylene, *p*-cymene, phenanthrene, and *p*- and *o*-nitrotoluene. The *p*-cymene

¹⁾ Chem. Weekblad 8 (1911), 651. Quoted from Chem. Zentralbl. 1911, II. 1029.

²⁾ Comp. Report October 1907, 123; October 1909, 159; October 1911, 122.

³⁾ Berl. Berichte 45 (1912), 38.

was exposed to light from June 13., 1911 to November 13., 1911 in 5 bottles, each of 1 litre capacity, filled with oxygen. Each bottle contained 15 grams cymene and 100 cc. water. When the bottles were opened a considerable vacuum was found, which had been caused by the consumption of oxygen. The reaction-liquid, which gave an acid reaction, was found to contain *p*-cuminic acid (m. p. 119°), methovinylic benzoic acid (m. p. 165°), and *p*- α -hydroxyisopropyl benzoic acid. Experiments carried on in the dark showed no auto-oxidation.

Pharmaco-physiological Notes.

In a lecture by H. Emde¹⁾ it is stated that the chemistry of the essential oils affords many examples of Loew's well-known law that bodies with double bonds are more poisonous than the corresponding saturated bodies. For instance, the toxicity of allyl sulphocyanide is much greater than that of the corresponding saturated compound. The influence of the position of the double bond upon toxicity may also be seen in the safrol series. Safrol, with its allyl-group, is considerably more poisonous than is *iso*-safrol with the propenyl group in the side-chain. Chemically, the phenyl-allyl compounds react much more readily than the corresponding propenyl compounds; in the latter the double bond is conjugated with the double bond of the benzene nucleus; in the former it is not.

Among the terpenic bodies, pulegone causes fatty degeneration of the organs and phosphorism, while menthone, which is derived from the addition of hydrogen to the double bond of pulegone, is much less poisonous. Its physiological action also is less pronounced than that of carvone, which has a double bond in the side-chain.

It is also stated that the allyl ethers myristicine, apiol and 1-allyl-2,3,4,5-tetramethoxy benzene, which possess a pronounced physiological action, owe their toxicity in part to their unsaturated side-chain.

H. Fühner²⁾ has investigated the ratio of activity of the following univalent alcohols, *viz.*, methylalcohol, ethylalcohol, *n*-propylalcohol, *n*-butylalcohol, *n*-amylalcohol, *n*-hexylalcohol, *n*-heptylalcohol and *n*-octylalcohol upon erythrocytes, sea-urchins' eggs, convoluta and phoxinus.

Phyto-physiological Notes.

The *Atti R. Accad. dei Lincei, Roma* (5), 20 (1911), II. p. 349, of which Sig. I. Giglioli³⁾ has kindly sent us a copy, contain an article from his pen on the probable function of the essential oils and other volatile con-

¹⁾ Apotheker Ztg. 26 (1911), 785.

²⁾ Zeitschrift für Biologie 57 (1912), 465. From a reprint kindly sent to us.

³⁾ Quoted from Chem. Zentralbl. 1912, I. 271.

stituents of plants as the cause of the movement of the juices in the vegetable tissues. According to the author's theory the essential oil, by affecting the surface-tension of the water, causes a movement in the plant-juices containing the enzymes, or the substances in which the enzymes are capable of effecting a change. This movement produces enzymatic reactions, in the course of which certain special bodies undergo decomposition, which in turn results in an increase of osmotic pressure, causing a renewed flow of water. In fact, the accumulation of water in the tissues is frequently connected with enzymatic action, as the author has already demonstrated on previous occasions. Not only chloroform, benzene, toluene and other compounds, but also many essential oils increase the juiciness of the tissues by allowing the water to vacate the cells and by driving the plant-juice through membranes which under other conditions it is unable to penetrate. Besides water certain other readily hydrolysable compounds are split-off, simultaneously with enzymes, which possess the power of resolving complex into simple compounds. These processes again cause fresh accumulations and movements of the water. Dried, compressed yeast, when exposed to the action of chloroform, eucalyptus oil, camphor oil, or camphor becomes soft within the course of a few hours, and after a few days it is possible to filter the juice through paper or porous porcelain. This juice contains zymase and produces alcoholic fermentation in solutions of cane-sugar or glucose. Zymase is more easily obtainable by this process than by the familiar methods. The process may also be usefully applied in the study of the toxicity of fungi and other vegetable substances. Giglioli, for instance, has tested the action of 128 essential oils and other volatile bodies upon green, newly-gathered cherry-laurel leaves, and has found that in almost every instance hydrocyanic acid was liberated¹⁾. The author surmises that all aromatic substances which are generated in plants would set up a similar movement of the juices in cherry-laurel leaves. According to Giglioli the part played by the essential oils in the organism of the conifers consists of promoting the flow of water through the cells and membranes, of acting as carriers of enzymes and soluble constituents and of causing enzymatic action by which the movement of the juices is favoured and increased.

The oil content of several different plants has been determined at Buitenzorg²⁾ as follows: 50 kilos green peel of *Djeroek dalima* yielded 2,7 cc. oil; 7,5 kilos dry buds of *Gnaphalium javanicum*³⁾ contained 3,5 cc.

¹⁾ Similar observations on the action of volatile bodies upon plants which contain odorous substances in the form of glucoside-compounds have been quoted by us on previous occasions. Comp. Report April 1910, 161; April 1911, 159.

²⁾ Jaarb. dep. landb. in Ned.-Indië, Batavia 1910, 50.

³⁾ *Gnaphalium javanicum*, Reinw. = *Antennaria javanica*, D. C. (according to the *Index Kewensis*).

of an oil with a terpene-like odour; 5,15 kilos pelargonium branches (a hybrid of *Pelargonium Radula*, l'Hérit. and *P. graveolens*, l'Hérit.) when distilled yielded 3 cc. oil; 5 kilos leaves of *Dryobalanops aromatica*, Gaertn. yielded 54 cc. oil.

On p. 41 of the present Report we refer to Brooks's discovery of the occurrence of an oxidase in the flowers of *Michelia Champaca*. Brooks¹⁾ has discovered the presence of enzymes with an oxidative action not only in the above-named flowers, but in many other plants yielding volatile oils and it would appear as if these bodies were of considerable importance in the formation of certain constituents of essential oils. For example, Lecomte²⁾ surmises that in the vanilla-plant coniferyl alcohol is converted by an oxidase into vanillin. The fact that the menthone in the peppermint herb and the carvone in the caraway plant are principally formed only during the flowering-season, points to the probability that the generation of these oxygenated bodies is connected with the presence of an oxidative enzyme. As a matter of fact, Brooks has succeeded in tracing the occurrence of oxidase in the peppermint herb and in several other plants.

In order to establish this fact, the fresh plants were ground with clean quartz sand and a little water to the consistency of a paste, from which he pressed a juice. This he tested with several reagents (guaiac resin, pyrogallol, phenolphthalein) for the presence of enzymes with an oxidative action, and thus he succeeded in demonstrating the occurrence of an oxidase in the pressed juice of green caraway fruit. In the peppermint herb the enzymes with oxidative action occur chiefly in the inflorescence; the oxidase-reactions being very feeble with non-flowering plants. In addition to *Mentha piperita*, the author obtained active extracts from *Mentha viridis*, *M. crispa*, *M. sylvestris* and *M. gentilis*. The peppermint herb contains a catalase as well as an oxidase. 25 g. Peppermint flowers yielded 25 cc. extract, of which 5 cc. liberated 42 cc. oxygen from 10 cc. 3% hydrogen peroxide solution within the space of 6 minutes. Valerian root contains an enzyme (lipase) which splits up fatty bodies. Brooks has also established oxidase in tansy leaves, in the leaves of *Thuja occidentalis*, and in the herb of *Satureja montana* and of *Calamintha officinalis*.

With roses and with palmarosa grass the test for oxidases resulted negatively, and this explains why the oils of these plants contain large proportions of alcohols and but little aldehydes.

The fact that the scent of many flowers deteriorates shortly after the gathering gives rise to the surmise that the flowers contain oxidases. Brooks is of opinion that flowers of this kind are not well suited for enfleurage.

¹⁾ Journ. Americ. chem. Soc. 34 (1912), 67.

²⁾ Compt. rend. 133 (1901), 745; Journ. de Pharm. et Chim. 17 (1903), 341; Comp. Report October 1903, 104.

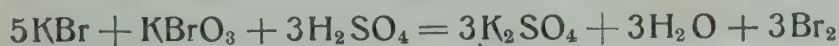
In our April Report of 1911, p. 167, we mentioned that Klobb, Garnier and Ehrwein had recovered hydrocarbons from the dried flowers of a large number of plants. Klobb¹⁾, after removing the hydrocarbons, has isolated from the ethereal or alcoholic extract of the flowers of *Matricaria Chamomilla*, *Tilia europæa*, *Linaria vulgaris* and *Verbascum Thapsus*, *l*-phytosterols possessing the following melting-points: 120 to 131°, 126°, 133 to 138° and 142 to 144°.

In our last Report (p. 124) we stated that Sack had detected the presence of indole in the flowers of various *Citrus*-species. We gather from the *Apotheker Zeitung*²⁾ that Sack has also found the same body in the aroma of the flowers of *Citrus Medica*, L. and *C. Limetta*, Risso.

F. Horton and E. F. and H. E. Armstrong³⁾ report on a glucoside of *Lotus corniculatus*, L. (N. O. Leguminosæ) which splits off hydrocyanic acid. The glucoside is generally accompanied by an enzyme. *Lotus corniculatus* var. *major* contains neither glucoside nor enzyme.

Chemical Notes.

With the object of discovering a standard for the unsaturated character of hydroaromatic compounds, J. Klimont and W. Neumann⁴⁾ have investigated the conditions under which the absorption of bromine by unsaturated compounds takes place quantitatively. Working according to the equation



good results were obtained. The generation of halogen oxide compounds is prevented by adding sulphuric acid. The determination is carried out by dissolving a few decigram of the terpene in chloroform, diluting the mixture with a known quantity of an aqueous solution of potassium bromide and potassium bromate in the proportions indicated by the above equation, adding sulphuric acid (1:2) and shaking. Iodide of potassium is then added in excess and the iodine liberated is titrated.

Hydrocarbons.

A paper by A. F. Sievers⁵⁾ on the absorption of organic acids by unsaturated hydrocarbons contains some interesting data on the behaviour of these acids, particularly glacial acetic acid, towards pinene and limonene.

¹⁾ Annal. de Chim. et Phys. (8), 24 (1911), 410. Quoted from Chem. Zentralbl. 1912, I. 87.

²⁾ Pharm. Weekblad 48 (1911), 48, 307. Quoted from Apotheker Ztg. 26 (1911), 836.

³⁾ Chem. News 104 (1911), 276. Quoted from Pharmaceutical Journ. 87 (1911), 81.

⁴⁾ Pharm. Post 44 (1911), 587. Quoted from Chem. Zentralbl. 1911, II. 953.

⁵⁾ Bull. of the Univers. of Wisconsin, Science Series, 4 (1911), 39 (No. 434). From a reprint kindly sent to us.

Table I.

Mixture consisting of	Date	d_{20}°	$[\alpha]_{20}^{\circ}$	% Ester calc. as pinene- or limonene- "acetate"
1 vol. ¹⁾ pinene + 1 vol. glacial acetic acid . .	27. 8. 06	0,9400	+ 8° 31'	0
	1. 11. 06	0,9450	+ 7° 50'	2,09
	13. 12. 06	0,9460	+ 7° 45'	3,32
	15. 5. 07	0,9502	+ 7° 18'	7,40
	7. 12. 09	0,9590	+ 3° 15'	18,3
1 vol. pinene + 2 vols. glacial acetic acid . .	27. 8. 06	0,9744	+ 6° 8'	0
	1. 11. 06	0,9769	+ 4° 50'	3,03
	13. 12. 06	0,9785	+ 4° 35'	4,83
	15. 5. 07	0,9804	+ 4° 15'	9,05
	7. 12. 09	0,9960	+ 2° 13'	28,70
1 vol. limonene + 1 vol. glacial acetic acid . .	29. 11. 06	0,9380	+ 47° 30'	0
	4. 1. 07	0,9388	+ 47° 10'	1,00
	15. 3. 07	0,9392	+ 47° 32'	1,82
	15. 5. 07	0,9400	+ 47° 0'	2,06
	7. 12. 09	0,9470	+ 38° 39'	12,90
1 vol. limonene + 2 vols. glacial acetic acid . .	29. 11. 06	0,9733	+ 31° 52'	0
	4. 1. 07	0,9737	+ 31° 0'	0,89
	15. 3. 07	0,9744	+ 31° 25'	2,84
	15. 5. 07	0,9748	+ 31° 43'	2,74
	7. 12. 09	0,9880	+ 28° 42'	10,07
1 vol. limonene + 1 vol. glacial acetic acid + 1,11 g. HCl	29. 11. 06	0,9390	+ 47° 35'	0
	4. 1. 07	0,9403	+ 47° 20'	1,68
	15. 3. 07	0,9402	+ 47° 38'	2,93
	15. 5. 07	0,9408	+ 46° 45'	2,78
	7. 12. 09	0,9430	+ 46° 16'	7,47
1 vol. limonene + 2 vols. glacial acetic acid + 1,11 g. HCl	29. 11. 06	0,9742	+ 31° 50'	0
	4. 1. 07	0,9750	+ 31° 30'	2,23
	15. 3. 07	0,9750	+ 31° 20'	3,14
	15. 5. 07	0,9754	+ 31° 25'	3,78
	7. 12. 09	0,9770	+ 30° 20'	9,39
1 vol. limonene + 1 vol. glacial acetic acid + 2,5 g. dehydrated so- dium acetate	29. 11. 06	0,9414	+ 47° 40'	0
	4. 1. 07	0,9440	+ 46° 25'	1,26
	15. 3. 07	0,9464	+ 46° 0'	2,88
	15. 5. 07	0,9490	+ 45° 15'	5,19
	7. 12. 09	0,9700	+ 35° 45'	33,30
1 vol. limonene + 2 vols. glacial acetic acid + 2,5 g. dehydrated so- dium acetate	29. 11. 06	0,9758	+ 31° 50'	0
	4. 1. 07	0,9758	+ 31° 4'	1,18
	15. 3. 07	0,9785	+ 31° 0'	3,15
	15. 5. 07	0,9798	+ 31° 12'	5,70
	7. 12. 09	0,9870	+ 28° 58'	15,95

¹⁾ 500 cc.

Table II. Heating in pressure-bottles.

Mixture consisting of	Period of Heating	$d_{20^{\circ}}$	$[\alpha]_{D20^{\circ}}$	% Ester	Temperature
1 vol. pinene + 1 vol. glacial acetic acid . .	8 hours	0,9465	+ 4° 25'	5,80	100°
	24 "	0,9502	+ 3° 40'	8,37	100°
1 vol. pinene + 2 vols. glacial acetic acid . .	8 hours	0,9807	+ 2° 33'	8,58	100°
	24 "	0,9838	+ 2° 36'	13,12	100°
1 vol. pinene + 1 vol. glacial acetic acid . .	8 hours	0,9590	+ 4° 24'	18,78	140—150°
	24 "	0,9568	+ 3° 52'	18,90	140—150°
1 vol. pinene + 2 vols. glacial acetic acid . .	8 hours	0,9962	+ 2° 35'	25,50	140—150°
	24 "	0,9881	+ 1° 30'	25,40	140—150°
1 vol. pinene + 1 vol. glacial acetic acid . .	8 hours	0,9517	+ 3° 0'	11,5	175—185°
	24 "	0,9581	+ 3° 18'	19,1	175—185°
1 vol. pinene + 2 vol. glacial acetic acid . .	8 hours	0,9895	+ 2° 37'	11,5	175—185°
	24 "	0,9876	+ 1° 23'	25,3	175—185°

Heating with a reflux-condenser.

1 vol. pinene + 1 vol. glacial acetic acid . .	—	—	—	1,37	—
	15 min.	—	—	1,99	—
	1 hour	—	—	4,82	—
	20 "	—	—	19,61	—
1 vol. pinene + 2 vols. glacial acetic acid . .	—	—	—	2,39	—
	15 min.	—	—	7,46	—
	1 hour	—	—	8,75	—
	20 "	—	—	24,80	—

Sievers prepared a set of mixtures of pinene with equal and with double quantities by volume of glacial acetic acid, and a corresponding set of limonene mixtures. In some of the latter he introduced into the solution a known weight of hydrogen chloride. Finally, Sievers made experiments with limonene with an equal and a double volume of glacial acetic acid with the addition of a known weight of sodium acetate. The density, rotation, and ester value of these mixtures were repeatedly determined within a period of from 7 to 9 months, and again after 2½ years. Part of the figures ascertained by Sievers are reproduced in table (I) (p. 166) below.

The figures in the above table show that by adding sodium acetate pinene and limonene are more ready to combine with acetic acid than is the case when adding hydrochloric acid.

The pinene was heated with glacial acetic acid in pressure-bottles at high temperatures and the ester of these mixtures was determined.

According to Sievers the reactions which take place at room-temperature are due to simple absorption, whereas at high temperatures the acid unquestionably attacks the molecule. The same experiments were repeated at atmospheric pressure by heating in a reflux condenser. In both cases the ester value was found to be much higher than in the previous experiments. A few of the values determined by Sievers are given in the table (II) (p. 167) below.

The findings of Sievers described above made it appear desirable to determine the extent to which acetic anhydride reacts with pinene and limonene under experimental conditions similar to those observed in acetylating essential oils. Several samples of freshly purified and rectified terpenes, when treated in this manner, gave an ester value after acetylation of not more than $1,8 = 0,5\%$ $C_{10}H_{18}O$, a value which is negligible in practice, and is therefore without effect in the alcohol-determination of essential oils. The values are slightly higher with impure hydrocarbons, or hydrocarbons which are somewhat resinified as a result of prolonged keeping. Where such was the case we observed an ester value after acetylation ranging, according to the age of the sample, up to $15 = 4,2\%$ $C_{10}H_{18}O$; a pinene which was more than four years old registering as much as $38,2 = 10,8\%$ $C_{10}H_{18}O$.

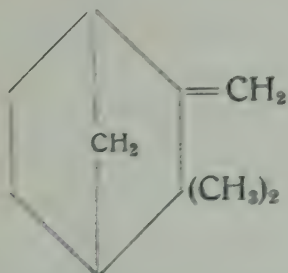
Camphene. K. Auwers¹⁾ in a paper on the constitution of camphene, refers to the recent work of Aschan and Lipp²⁾ on this hydrocarbon. The progress attained by the researches embodied in that work lies in the proof which has been afforded that, contrary to the opinions of Moycho and Zienkowsky, the camphenes of different origin are in their essentials of a uniform character and represent one and the same hydrocarbon. In the present state of our knowledge however it appears to be impossible to draw positive conclusions with regard to the constitution of the hydrocarbon from the chemical conversions of camphene alone. But in the case under review it would appear that the spectrochemical behaviour scarcely leaves room for doubt as to the group of hydroaromatic compounds to which the hydrocarbon belongs. To obtain useful results it is necessary, when calculating the spectrochemical data, to compare the latter with water at 4° . In comparing the statements of Wallach, Brühl, Eijkman, and Heile on the refraction and density of camphene, it will be found that they have all been estimated at temperatures ranging from 40 to 78° , but the estimated values may be converted with sufficient accuracy to 50° . Having done this, Auwers ascertained the mean of the camphene-values found by the above-mentioned authors to be $M_d 43,73$ and

¹⁾ Liebigs Annalen 387 (1912), 240.

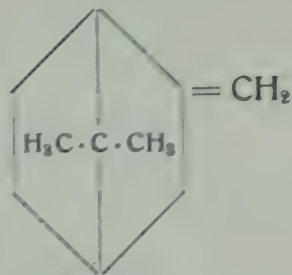
²⁾ Comp. Report April 1911, 188; October 1911, 132, 135.

M_D 44,02. These results show that it is practically certain that camphene cannot be a saturated body with a tricyclic ring, because the excess of the ascertained mean values of refraction over the values calculated for the saturated formula $C_{10}H_{16}$ is not less than $+2,12$ and $+2,14$. It is true that a tricyclic ring also effects a rise in refraction but not by far to such an extent as indicated in these excess-values. From the observations on cyclene, β -bornylene and β -pinolene, all of which are saturated tricyclic compounds, it is clear that in a tricyclic system the tricyclic ring claims a similar, and apparently only slightly larger increment than in other cyclical bodies. From the spectrochemical observations which have been made within the past few years it may be stated with certainty that camphene cannot be a saturated compound. The examination of seven different camphene-preparations has shown the molecular refraction of camphene to be larger than that calculated for the formula $C_{10}H_{16}$, and the exaltations to equal $E\Sigma_\alpha + 0,32$ and $E\Sigma_D + 0,37$. This behaviour points to the semicyclic structure of camphene, and would appear to afford spectrochemical proof of the corrections of Wagner's camphene formula.

What has been stated above with regard to camphene is also applicable to *D*-*l*-fenchene and to its optical antipode, *L*-*d*-fenchene. Here, $E\Sigma_D = +0,33$, a fact which can only be explained on the hypothesis of a semicyclic double linking. Accordingly, the formula of *D*-*l*-fenchene would be that given by Wallach and almost universally accepted.



Wagner's Camphene-formula.



D-*l*-fenchene.

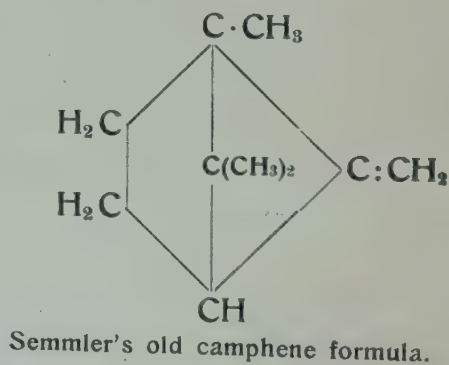
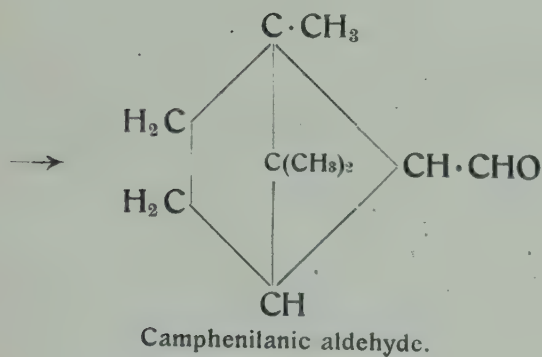
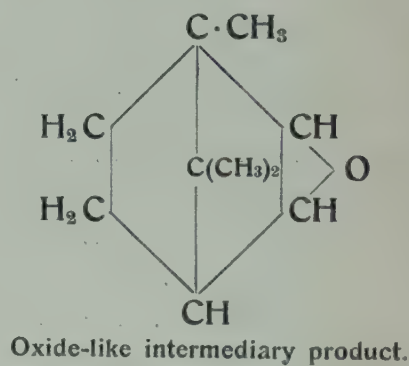
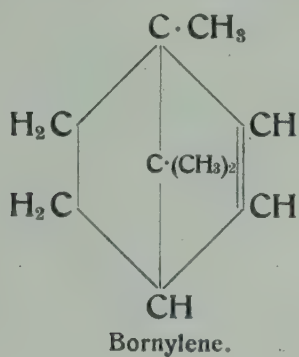
G. G. Henderson and Miss M. M. J. Sutherland¹⁾ have described as camphylic acid an acid which they had obtained from camphene by oxidising it with hydrogen peroxide. In a supplementary notice they state²⁾ that Brecht has called their attention to the fact that Perkin had also applied the name of camphylic acid to the acid obtained by him by fusing sulphocamphylic acid with alkalies. Moreover, Aschan informed them that an acid apparently identical with camphylic acid had been obtained by him by oxidising camphene with potassium permanganate at a low temperature in acetic acid solution, and that he has suggested the name

¹⁾ Comp. Report October 1911, 134.

²⁾ Proceed. chem. Soc. 27 (1911), 279.

of "camphenanic acid" for this body. As a result of these communication Henderson and Miss Sutherland announce that they will in future call their camphylic acid "camphenanic acid".

Bornylene. As stated on p. 171, the conversion of bornylene into camphenilanaldehyde points to the close relationship of the camphene and bornylene nuclei. According to G. G. Henderson and I. M. Heilbron¹⁾ the conversion may be represented by the formulæ given below, it being assumed that an oxide-like body is formed as an intermediary product. On the basis of this conversion, as well of theoretical consideration which we have not space to repeat here, the authors regard Semmler's old camphene-formula as the most likely to be correct.



G. G. Henderson²⁾, who, with various collaborators, had previously investigated the action of chromyl chloride upon limonene, pinene, and terpinene, has recently, together with I. M. Heilbron³⁾, oxidised bornylene with chromyl chloride and has also studied the behaviour of the hydrocarbon when attacked by nitric and nitrous acids. Reaction of chromyl chloride with bornylene which had been dissolved in carbon disulphide, gave rise in the first place to an additive product $C_{10}H_{16}, 2Cr_2O_2Cl_2$, which upon the addition of ice was converted into a chloroketone $C_{10}H_{15}OCl$.

¹⁾ Journ. chem. Soc. 99 (1911), 1901.

²⁾ Comp. Report April 1908, 180; November 1908, 171; October 1909, 176.

³⁾ Journ. chem. Soc. 99 (1911), 1887.

and an aldehyde $C_9H_{15}CHO$. The chloroketone proved to be a hitherto unknown chlorocamphor, of which the semicarbazone melted at 234 to 235° , and yielded camphoric acid when oxidised with permanganate of potassium, and camphor when heated with alcoholic potash liquor in a sealed tube at 150 to 160° . The aldehyde $C_9H_{15}CHO$ could be purified from the primarily produced bisulphite-compound, and was identified as camphenilanic aldehyde. This aldehyde being a true camphene derivative, its generation from bornylene points to the relationship of this hydrocarbon with camphene. When exposed to air, camphenilanaldehyde was oxidised to a mixture of camphenilanic acid (m. p. 65°) and *isocamphenilanic acid* (m. p. 118°). Camphenilanic acid is very readily converted into the *iso*-modification, repeated recrystallisation from water, alcohol or light petroleum being sufficient to effect the conversion. When semicarbazide is allowed to act upon camphenilanaldehyde, *isocamphenilanaldehyde semicarbazone* (m. p. 191 to 192°) is formed. Bromo*isocamphenilanic acid* (m. p. 204 to 205°) was prepared by the authors by heating *isocamphenilanic chloride* with bromine under pressure, and decomposing the brominated chloride with water. Heating bromo*isocamphenilanic acid* with aqueous soda solution gave rise to an unsaturated acid $C_9H_{13}\cdot CO_2H$ (m. p. 147°).

Henderson and Heilbron also acted with nitrous acid upon bornylene, by overlaying concentrated aqueous sodium nitrite solution with a solution of bornylene in light petroleum, and gradually adding glacial acetic acid. They obtained the following reaction-products: 1. Bornylene nitrosite ($C_{10}H_{16}N_2O_3$)₂, m. p. 163° , which was oxidised into camphoric acid. 2. An oily liquid, perhaps bornylene *isonitrosite*. 3. Camphorquinone (m. p. 197 to 198°) and 4. a crystalline body, m. p. 84 to 85° , perhaps a bornylene nitrite. With nitric acid, bornylene was oxidised into a mixture of camphoric acid and a body $C_{10}H_{16}O_4N_2$, crystallising in yellow needles, which was identified as to be a dinitrocamphane.

The bornylene employed for these reactions was prepared by Tschugaeff's method from borneol from primarily-produced bornyl methylxanthogenate.

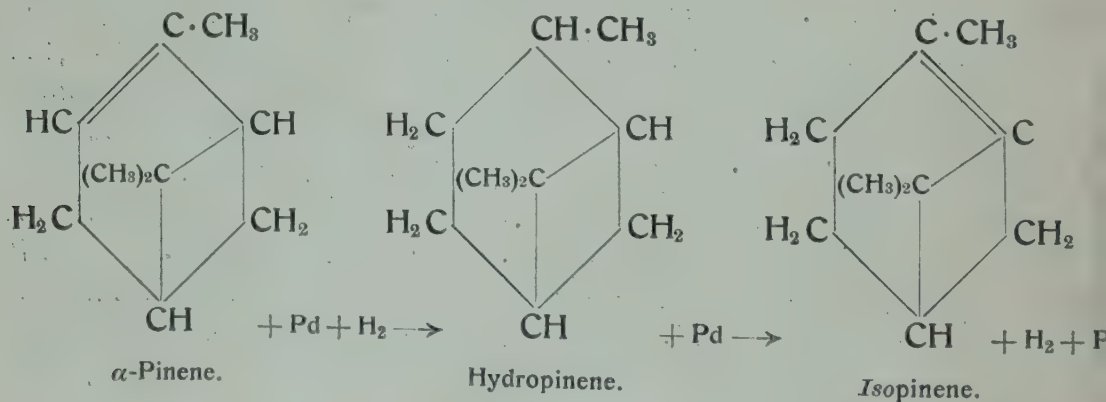
On the constitution of *D-l*-fenchene see p. 169.

α -Pinene. Mario Mayer¹⁾ has published an historical résumé of the researches into pinene, and of the relations of pinene to camphor and to other bodies of similar chemical structure. From its nature it follows that the publication is chiefly retrospective and that the new experimental material contained in it is of subordinate interest, the principal reference of this character being that dealing with the splitting-up of the hydroxylamine oxime of *l*- α -pinene by means of α -bromo- π -camphor sulpho-acid.

¹⁾ *Tesi di libera docenza, R. Istituto di Studi sup.*, Florence 1911. Our best thanks are due to the author for kindly sending us a copy of the pamphlet.

The author has succeeded in converting the inactive hydroxylamine oxime (decomposition-point 140°), into two salts of the acid in question (decomposition-points 195 and 172° respectively). When the salts were resolved with soda they gave rise respectively to a dextrorotatory and a levorotatory oxime, decomp. pts. 147 and 145° , $[\alpha]_D$ in methylalcoholic solution $+60,74$ and $-59,66^{\circ}$.

Isopinene. N. Zelinsky¹⁾ describes *isopinene*, a hydrocarbon which is an isomeride of α -pinene. With the object of preparing this body, *l*- α -pinene (b. p. 155 to $155,5^{\circ}$; d_{40}^{20} $0,8587$; $[\alpha]_D -43,81^{\circ}$; n_{D20} $1,4652$) in absolute ethereal solution was allowed to react with palladium black. After a few hours, hydrogen was passed into the liquid at ordinary temperature, giving rise to *isopinene* possessing the following constants: b. p. $158,5$ to $159,5^{\circ}$; d_{40}^{20} $0,8573$, $[\alpha]_D -38,09^{\circ}$, n_{D20} $1,4641$. Neither hydrochloride nor nitrosoc chloride is formed. Zelinsky assumes that α -pinene first absorbs hydrogen under formation of *hydropinene*, and that *isopinene* results from the latter somewhat after the following reaction: —



The behaviour of α -pinene towards palladium black is very different when it is exposed for a period of 4 weeks to the action of hydrogen under very low pressure. In this case it yields *hydropinene* (b. p. 167 , to 168° ; d_{40}^{20} $0,8567$; $[\alpha]_D -19,84^{\circ}$; n_{D20} $1,4605$). When reducing α -pinene by Sabatier's method, the author obtained a mixture of two hydrocarbons (b. p. $163,5$ to 165° and 168 to $168,5^{\circ}$).

Isopinene, the hydrocarbon which was described by Aschan²⁾ a few years ago, is not identical with Zelinsky's *isopinene*, as is evident from a comparison of the constants, as well as from the structural formulæ given by the respective authors. Apparently Zelinsky has overlooked Aschan's publication, otherwise he would certainly have named his hydrocarbon differently.

¹⁾ Berl. Berichte **44** (1911), 2782.

²⁾ Berl. Berichte **40** (1907), 2250; Öfversigt af Finska Vetenskaps-Societets Förhandlingar **51**, 1. Afd. A, Nr. 9. Comp. Report October 1907, 136; October 1909, 169.

Menthadiene. Some years ago we reported that Brunel¹⁾ has obtained a menthene by heating thymomenthol with bisulphate of potassium or phosphorus pentoxide. In view of the fact that the process of eliminating water by the aid of these reagents tends to bring about intramolecular rearrangements, G. G. Henderson and R. Boyd²⁾ have synthesised this menthene by heating thymomenthol with an aqueous solution of oxalic acid, thereby obviating the risk of intramolecular rearrangements. The Δ^3 -menthene prepared by this method had the same properties as Brunel's thymomenthene: b. p. 167 to 169°, d_{20}^{20} 0,8188, n_D 1,45363. It yields a nitrosochloride, m. p. 133°. With bromine a dibromide is formed, from which, when boiled with an excess of alcoholic potash liquor, a menthadiene (m. p. 173,5; d_{20}^{20} 0,8337; n_D 1,46539) results. This is probably a $\Delta^{2,4}$ -menthadiene. As it was interesting to compare the terpenes with isomeric hydrocarbons $C_{10}H_{16}$, Henderson and Boyd prepared 1,3-diethylcyclohexadiene from phenol, by converting phenol into 3,5-diethylphenol, and reducing the latter to 1,3-diethylcyclohexanol. Boiling diethylcyclohexanol with oxalic acid solution gave rise to a mixture consisting for the greater part of 1,3-diethylcyclohexene, contaminated with diethylcyclohexadiene. This mixture was converted into diethylcyclohexene dibromide, from which, when boiled with an excess of alcoholic potash liquor 1,3-diethylcyclohexadiene (b. p. 166 to 168°; d_{20}^{20} 0,8659; n_D 1,47575) resulted. The double bond is probably in the 3,5-position.

Cedrene. A few years ago Semmler and Hoffmann³⁾, while oxidising cedrene with permanganate of potassium in acetone solution, obtained a keto aldehyde or a diketone, together with a cedrene keto acid. In order to gain further insight into the molecular structure of cedrene, Semmler and F. Risse⁴⁾, have now subjected fairly large quantities of cedrene to oxidation with ozone in glacial acetic acid, as a result of which they obtained oxidation products which in many respects were similar to those prepared with permanganate of potassium. The cedrene employed in the oxidation process boiled between 123 and 124° (12 mm.). The neutral oxidation products formed consisted of a ketone $C_{14}H_{24}O$ or $C_{14}H_{22}O$ (m. p. of the semicarbazone 218°), and a keto aldehyde $C_{15}H_{24}O_2$. If the ketone possessed the formula $C_{14}H_{22}O$, it would follow that, in addition to the cedrene which was not saturated in the ring (from which only a ketone $C_{14}H_{24}O$ could originate), a semicyclic cedrene was admixed to the natural cedrene.

As an acid oxidation product an acid $C_{15}H_{24}O_3$, cedrene keto acid was isolated. The methyl ester of this acid possessed the following con-

¹⁾ Comp. Report April 1905, 103.

²⁾ Journ. chem. Soc. 99 (1911), 2159.

³⁾ Comp. Report April 1908, 28.

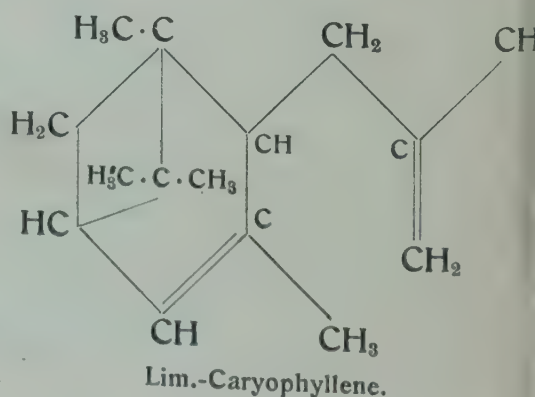
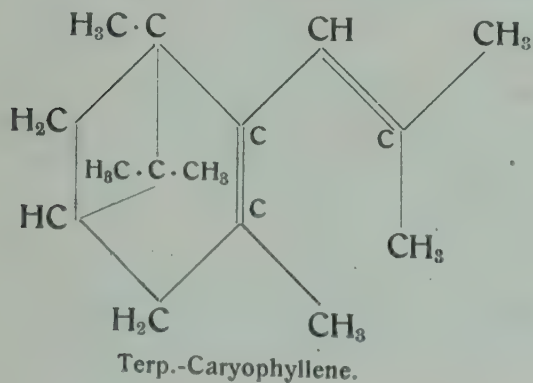
⁴⁾ Berl. Berichte 45 (1912), 355.

stants: b. p. 165 to 170° (10 mm.), $d_{20} 1,0509$, $\alpha_{D20} - 32^{\circ} 24'$, $n_D 1,488$. When oxidised with 27% nitric acid, cedrene keto acid yields an acid $C_{14}H_{22}O$ (m. p. 182,5°), to which the authors give the name of cedrene dicarboxylic acid, and of which the dimethylester had the following characters: b. p. 179 to 183° (13 mm.), $d_{20} 1,0778$, $\alpha_D - 31^{\circ} 36'$, $n_D 1,48084$.

The fact that cedrene keto acid $C_{15}H_{24}O_3$ is a methyl keto acid, which compares uniformly with dicarboxylic acid $C_{14}H_{22}O_4$ was confirmed by its giving rise to dicarboxylic acid when oxidised with alkaline bromine solution.

Semmler and Risse consider that the preparation of cedrene dicarboxylic acid $C_{14}H_{22}O_4$ affords an excellent means of detecting the presence of cedrene in essential oils.

Caryophyllene. So far, the santalols and santalenes were the only sesquiterpene bodies of which the structure was known, but recently Semmler and E. W. Mayer¹⁾ have succeeded in clearing up the principal outlines of the molecular structure of caryophyllene. As the researches of Deussen²⁾ have shown caryophyllene to consist of a mixture of several hydrocarbons, it was not an easy matter to elucidate the structure of the body. The proneness of caryophyllene to inversion renders its investigation extraordinarily difficult. For example, the authors look upon the compound $C_{14}H_{22}O$, which was obtained by Deussen and by Haarmann³⁾ in the course of oxidation with permanganate of potassium, as being not a derivative of the original caryophyllene, but a product of inversion, possibly of tricyclic *isocaryophyllene*. The only method by which useful results can be expected is oxidation with ozone, and as a matter of fact, Semmler and Mayer have succeeded, by gradually oxidising caryophyllene by means of ozone, in obtaining bodies which are in the main derived from two caryophyllenes. These they call *terp.-caryophyllene* and *lim.-caryophyllene*, and they assign to them for the present two formulæ which are analogous to those of terpinolene and limonene, as follows: —

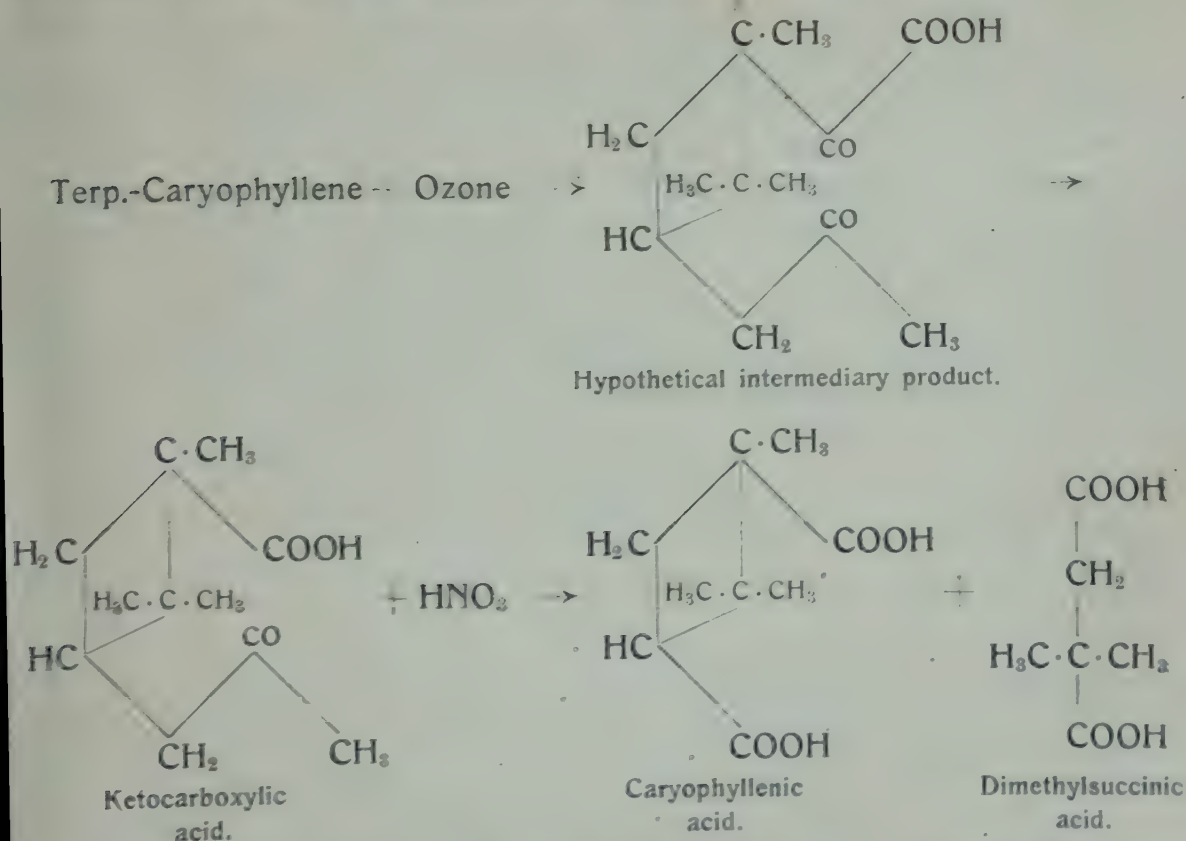


¹⁾ Berl. Berichte 44 (1911), 3657.

²⁾ Comp. Report November 1908, 176; April 1909, 124; October 1909, 177; April 1910, 167.

³⁾ Comp. Report October 1909, 177.

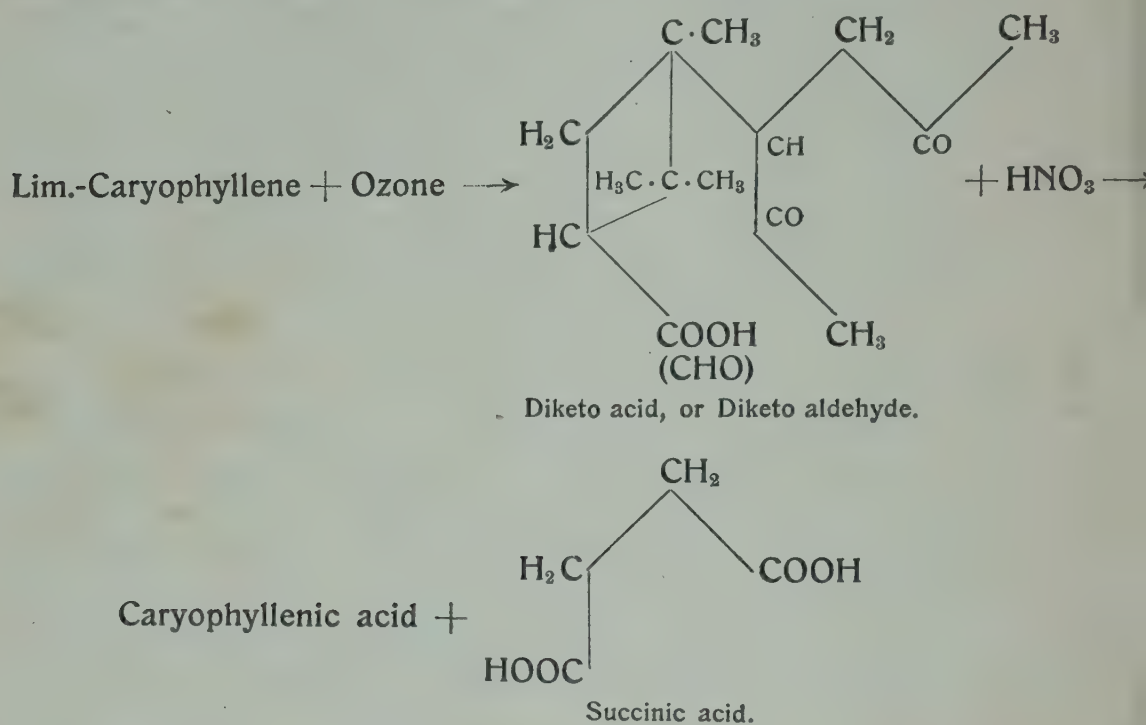
In the course of the ozonising process acid and neutral decomposition products were obtained. Among the former was a ketocarboxylic acid, $C_{11}H_{15}O_3$ (b. p. 183 to 187° at 11,5 mm.; m. p. of the semicarbazone 183°), and a diketocarboxylic acid $C_{14}H_{22}O_4$ (b. p. 229 to 232° at 11,5 mm.). The neutral decomposition products consisted of a ketone $C_{10}H_{15}O$ (b. p. 73 to 76° at 11,5 mm.; m. p. of the semicarbazone 176°), a diketone $C_{12}H_{20}O_2$ (b. p. 137 to 142° at 9 mm.; m. p. of the semicarbazone 219°) and a diketonaldehyde $C_{14}H_{22}O_3$ (b. p. 181 to 184° at 13 mm.). When oxidised with nitric acid the ketocarboxylic acid $C_{11}H_{15}O_3$ yielded a dicarboxylic acid $C_9H_{14}O_4$, b. p. 222 to 225° (13 mm.) to which the authors give the name of *caryophyllenic acid*. This body could not be obtained in the crystalline form, and the attempts made by us, at Semmler's suggestion, to crystallise the acid by strong cooling remained without result. Caryophyllenic acid closely resembles pinic acid, but, unlike the latter, it yields an anhydride (b. p. 152 to 158° at 10 mm.). The dimethyl ester of caryophyllenic acid gives the following constants: b. p. 127 to 131° (11 mm.), $d_{20} 1,0456$, $\alpha_{D20} + 44^\circ$, $n_{D20} 1,4462$. In addition to caryophyllenic acid the oxidation of the acid $C_{11}H_{15}O_3$ had yielded dimethyl succinic acid. The identical products of oxidation are obtained when the keto acid is treated with bromine solution. Semmler and Mayer conceive the generation of ketocarboxylic acid from the ozonide to proceed as follows: —



The diketocarboxylic acid $C_{14}H_{22}O_4$ was further oxidised with nitric acid, when it yielded an oil studded with crystals which proved to consist

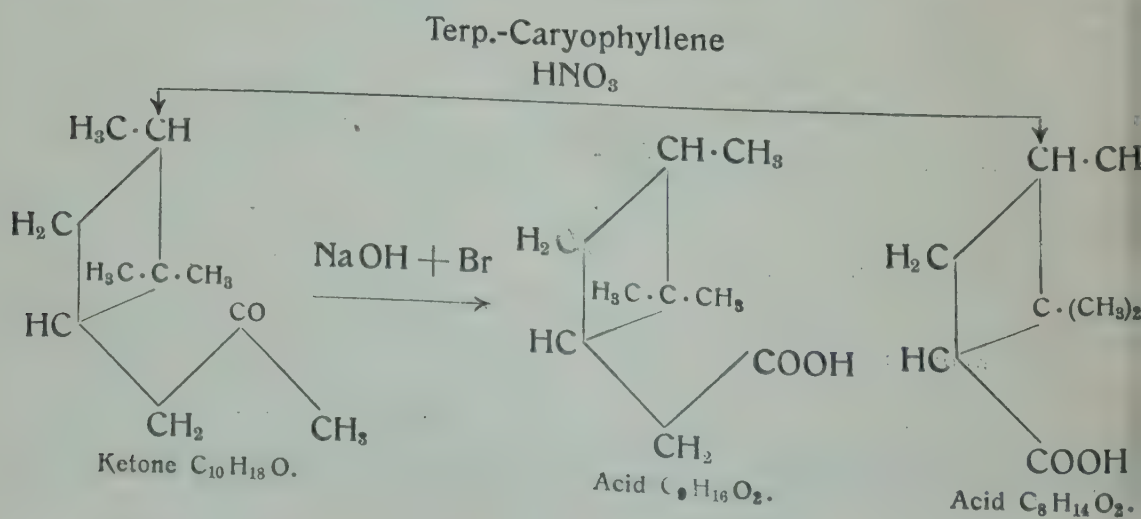
of succinic acid (m. p. 182°). When fractionated the oil yielded succinic anhydride as well as caryophyllenic acid.

The authors conceive the diketo acid to be a derivative of lim. caryophyllene, possibly according to the following reaction:—



In the course of the distillation of the acid oxidation products the first runnings consisted of an acid $C_8H_{14}O_2$, b. p. 120 to 128° (9 mm.), of which the amide had m. p. 96° .

The ketone $C_{10}H_{18}O$ referred to above, when oxidised with bromine solution, yielded an acid $C_9H_{16}O_2$ (b. p. 131 to 133° at 13,5 mm.; m. p. of the amide 114°). Oxidation with nitric acid resulted in an acid $C_8H_{14}O_2$ (b. p. 119 to 122° at 12 mm.; m. p. of the amide 115 to 116°). The author regards the ketone $C_{10}H_{18}O$ as a secondary decomposition product of the ozonisation, and as having the following genesis:—



When the diketone $C_{12}H_{20}O_2$ was oxidised with nitric acid or with an alkaline bromine solution it yielded dimethyl succinic acid and caryophyllenic acid. When oxidised with permanganate of potassium the diketo aldehyde was converted into the diketo acid $C_{14}H_{22}O_4$ mentioned above. Oxidation with nitric acid, as was to be expected, yielded caryophyllenic acid and succinic acid.

It follows from the investigations summarised above that the active caryophyllenes are not, as was thought by Deussen, derivatives of naphthalene, but of the terpenes or of systems allied to the latter.

In conclusion the authors report that they have converted caryophyllene prepared according to Deussen's method into its dihydrochloride (m. p. 68 to 69°), and that this product proved to be identical with the dihydrochloride from natural caryophyllene.

Reduction of the blue caryophyllene nitrosite with sodium and alcohol afforded a body $C_{15}H_{27}N$ (b. p. 148 to 150° at 13 mm.), which is probably an amine.

On the formation of hydrocarbons from hydrazine compounds, see p. 195.

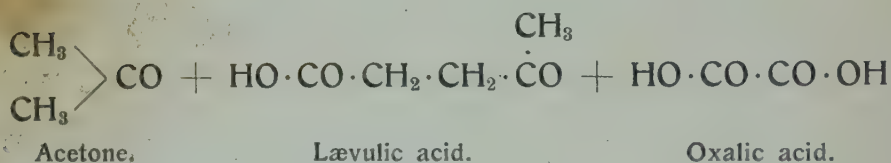
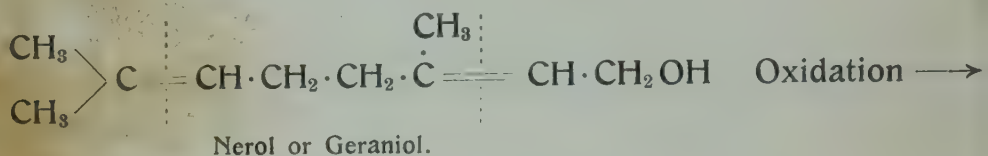
Alcohols.

Dihydrolinalool. In our last Report (p. 131) we described the alcohol dihydrolinalool, which was formed in hydrating dihydromyrcene. For purposes of comparison we had also prepared the alcohol synthetically from methylheptenone and magnesium ethyl iodide. The methylheptenone had been obtained both from citral (by oxidation), and from lemongrass oil (by treatment with bisulphite-solution). In view of the fact that, contrary to the experience with the product prepared from dihydromyrcene, we had obtained no phenylurethane with sharp m. p. from this dihydrolinalool, we also treated with magnesium ethyl iodide a methylheptenone which had been prepared by boiling citral with aqueous solution of carbonate of potassium according to Verley¹). But the dihydrolinalool prepared by this method likewise failed to yield a phenylurethane with a sharp m. p. Its constants, together with those of the products referred to above, are given in the subjoined table: —

Dihydrolinalool from	B. p.	d_{15}^0	n_{D15}^0	Mol. Refr.	
				Found	Calc.
Dihydromyrcene	92 to 92,5° (12 to 13 mm.)	0,8570	1,45531	49,47	49,438
Methylheptenone from citral (by oxidation) (B. p. 172,5 to 174°; d_{15}^0 0,8578)	77 to 78° (7 mm.)	0,8588	1,45641	49,46	49,438
Methylheptenone from lemongrass oil (B. p. 173 to 174°; d_{15}^0 0,8550; n_{D20}^0 1,43965)	66 to 66,5° (4 mm.)	0,8575	1,45661	49,558	49,438
Methylheptenone from citral (by boiling with solution of carbonate of potassium [B. p. 66° (15 mm.); d_{15}^0 0,8560; n_{D20}^0 1,44025]	67,5° (4 mm.)	0,8590	1,45611	49,424	49,438

¹) Bull. Soc. chim. III. 7 (1897), 175.

Nerol. Zeitschel¹⁾ has previously advanced the view that nerol is a stereoisomeride and not a structural isomeride of geraniol. Definite proof of the correctness of this theory has now been supplied by Blumann and Zeitschel²⁾ by the oxidative resolution of nerol by Tiemann and Semmler's method. In the course of this process acetone and lævulic acid were formed from nerol in the same quantitative proportions as from geraniol. The nerol used in the experiment had been prepared from oil of *Helichrys angustifolium* and possessed the following constants: b. p. 225 to 226°, $d_{15} 0.8815$, $\alpha_D + 0^\circ$, m. p. of the diphenylurethane 52 to 53°. The alcohol had first been oxidised with potassium permanganate solution and afterwards with chromic acid and sulphuric acid.



Menthol. Several years ago Brunel³⁾ showed that thymol was capable of being reduced to hexahydrothymol by Sabatier and Senderens' method. The complicated mixture which results from this conversion has been examined by R. H. Pickard and W. O. Littlebury⁴⁾, who have isolated from it several isomeric menthols and menthones, as well as 1-methyl-3-cyclohexanol. The thymol which had remained unchanged in the reduction process was removed from the reaction-product by treating with soda-liquor. After heating the mixture with phthalic anhydride in order to separate the alcohols, the ketones were isolated by means of semicarbazide. By repeated recrystallisation from 95% acetic acid the authors succeeded in separating two acid phthalates (m. p. 175 to 177° and 129 to 131° respectively), from the acids of the phthalic ester. The separation of the two esters is much facilitated when the dilute aqueous solution of the sodium salts is treated with magnesium chloride. The magnesium salt of the one ester is thereby precipitated in the form of a sparingly soluble compound which, after being recrystallised from alcohol, melts between 119 and 122°. When resolved with hydrochloric acid it yields the acid phthalic ester with m. p. 129 to 131°. When chloride of zinc is added to the filtrate of the magnesium salt, the zinc salt of the ester, m. p. 17

¹⁾ Berl. Berichte **39** (1906), 1780; Report October **1906**, 124.

²⁾ Berl. Berichte **44** (1911), 2591.

³⁾ Compt. rend. **140** (1905), 252; Report April **1905**, 103.

⁴⁾ Journ. chem. Soc. **101** (1912), 109.

to 177° is precipitated. The filtrate of the zinc salt, upon the addition of hydrochloric acid, yielded an acid phthalate, m. p. 93° , which may also be readily separated in the form of a calcium salt. The corresponding alcohol is 1-methyl-3-cyclohexanol: b. p. 173° (752 mm.), $d_{17}^{17^{\circ}}$ 0,912, m. p. of the phenylurethane 96° . The phthalate with m. p. 129 to 131° is that of the *i*-menthol with m. p. 34° (b. p. 103 to 105° at 16 mm.), which yields a phenylurethane, m. p. 104° and an acid succinate, m. p. 85 to 86° . To the alcohol corresponding to the acid phthalate with m. p. 175 to 177° the authors have given the name of *neomenthol*. This body melts at 51° and yields a phenylurethane with m. p. 114° and an acid succinate with m. p. 67 to 68° . *i*-Neomenthol is identical with the menthol (*isomenthol*) which has been obtained by Beckmann¹⁾ by hydrolysing *l*-menthylphenylurethane with sodium ethylate at 150° . The acid menthyl phthalate, m. p. 177° and the phthalic ester which has been prepared by Enklaar²⁾ from the alcohol which had been formed by the reduction of geraniol, are also probably identical with *i*-neomenthol. The menthol with m. p. 34° appears to be identical with Brunel's β -thymomenthol (*loc. cit.*) and with the menthol obtained by Kremers³⁾ in the reduction of a synthetical menthone.

The experiments with natural *l*-menthol made by Pickard and Littlebury have demonstrated the uniformity of this alcohol. From the brucine salt of the *l*-menthyl hydrogen phthalate they recovered *l*-menthol having a specific rotation of $-49,44^{\circ}$. The *i*-menthol with m. p. 34° was split up, from the primarily produced brucine salt and the cinchonine salt of the acid phthalate into *l*-menthol ($[\alpha]_D -48,27^{\circ}$; m. p. 42°) and *d*-menthol ($[\alpha]_D +48,15^{\circ}$; m. p. 40°). When splitting up *i*-neomenthol into its optical components the authors obtained *d*-neomenthol (b. p. 96° at 16 mm.; $[\alpha]_D +19,69^{\circ}$) and *l*-neomenthol (b. p. 105° at 21 mm.; $d_{40}^{20^{\circ}}$ 0,8995; $[\alpha]_{D18^{\circ}} -19,62^{\circ}$; $n_{D20} 1,46031$). Neither *d*- nor *l*-neomenthol was obtained in the solid state.

When oxidised with Beckmann's chromic acid mixture, *i*-menthol yielded *i*-menthone, b. p. 205° (748 mm.) which gave rise to an oxime, m. p. 80°) and a semicarbazone (m. p. 158°). The oxidation of *i*-neomenthol resulted in the same *i*-menthone. From *l*-menthol the authors obtained an *l*-menthone of somewhat higher rotatory power ($[\alpha]_{D19^{\circ}} -29,10^{\circ}$) than is stated in the literature on the subject ($[\alpha]_D -24,78$ to $28,18^{\circ}$). The oxidation of almost pure *d*-neomenthol led to the formation of an *l*-menthone (b. p. 204° at 750 mm.; $[\alpha]_{D19^{\circ}} 23,3^{\circ}$); *l*-neomenthol gave rise to *l*-menthone (b. p. 204° at 750 mm.; $[\alpha]_{D18^{\circ}} +24,85^{\circ}$). Both *d*-menthol and *i*-neomenthol, therefore, yield *d*-menthone, while *l*-menthol and *d*-neomenthol both yield *l*-menthone. An analogous result takes place in the case of *l*-borneol and *d*-isoborneol, which, when oxidised, give rise to camphor.

¹⁾ Journ. f. prakt. Chem. II. 55 (1897), 30.

²⁾ Berl. Berichte 41 (1908), 2086.

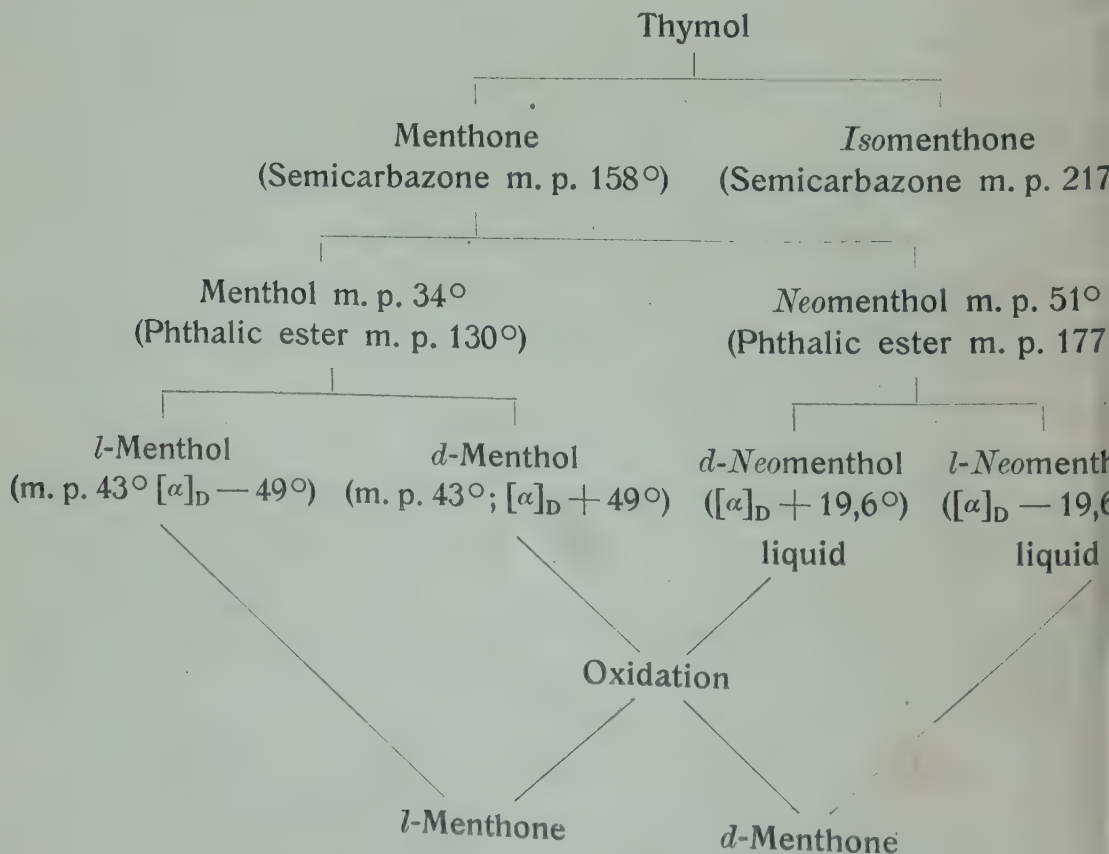
³⁾ Americ. chem. Journ. 18 (1896), 762.

Most interesting are the observations of Pickard and Littlebury on the occurrence of *neomenthol* in Japanese peppermint oil. At their request we had placed at their disposal a Japanese peppermint oil which had been freed from menthol as far as possible and which, after removal of the first and the last runnings, had been warmed with an equal quantity of benzoyl chloride. When the reaction was completed, and the hydrochloric acid had been removed by shaking with soda solution, menthone and other volatile substances were distilled off with steam. The residual ester when saponified, yielded a mixture of alcohols from which a fraction was obtained possessing the following characters: b. p. 80 to 82° (4 mm), $d_{15} 0.9032$, $\alpha_D - 8^\circ 48'$ (menthol-content about 90%).

The authors converted this menthol fraction into its acid phthalate which gave m. p. 140 to 143°, $[\alpha]_D + 4.58^\circ$. The ester was recrystallized 28 times from 95% acetic acid, after which it melted between 141 and 144°, the specific rotation being $+57.16^\circ$ (in chloroform). Mixed with *d*-neomenthyl phthalic ester, the ester melted between 142 and 144°. The alcohol which was regenerated from the ester, when oxidised with Beckmann chromic acid mixture, yielded *l*-menthone ($[\alpha]_D - 28.33^\circ$).

The odour of *d*- and *l*-neomenthol differs altogether from that of *d*- and *l*-menthol.

The following arrangement explains the reactions described by the authors: —



P. F. Frankland and H. H. Sullivan¹⁾, when reacting with ammonia upon menthyl chloroacetate, obtained the menthyl ester of Heintz' nitrilotriacetic acid²⁾ $N(CH_2 \cdot CO_2 \cdot C_{10}H_{19})_3$, a compound which crystallises in prismatic needles; m. p. 80,5°.

Fatty-aromatic alcohols. At the present time we possess three methods³⁾ for the preparation of a fatty-aromatic alcohol $X \cdot CH_2 \cdot OH$, or its halogen ester $X \cdot CH_2 \cdot Cl$ from the alcohol $X \cdot OH$ or halogenide $X \cdot Cl$. They are: first, condensation with cyanide of potassium, saponification of the nitrile $X \cdot CN$ into acid, esterification into the ester $X \cdot CO_2 C_2 H_5$ and reduction of this ester into the alcohol $X \cdot CH_2 OH$ according to Bouveault. Secondly, reaction with magnesium into $X \cdot MgCl$ and conversion into the alcohol $X \cdot CH_2 \cdot OH$ by means of trihydroxymethylene according to Grignard. Thirdly, reduction of the nitrile $X \cdot CN$ into the base $X \cdot CH_2 \cdot NH_2$ and conversion of the benzoyl-compound of the latter with phosphorus pentachloride into the chloride $X \cdot CH_2 Cl$ according to v. Braun. All three of these reactions (as v. Braun has discovered), are applicable to the halogen hydrogen esters of the phenylpropyl alcohol, but Grignard's method is the shortest and gives the highest yield of phenylbutyl alcohol. In the higher series the conditions undergo a change, inasmuch as the synthetic action of the magnesium is increased and the alcohol-yield reduced. Here the choice lies between Bouveault's and v. Braun's methods, of which the latter is also suitable for large quantities of material, while Bouveault's method answers only when comparatively small quantities are treated.

The following alcohols prepared by the author are of interest to us in their quality as homologues of phenylethyl alcohol: δ -phenylbutyl alcohol (b. p. 140° at 14 mm.; pronounced, but rather unpleasant odour) ϵ -phenylamyl alcohol (b. p. 155° at 20 mm.; has a pleasant lemon-like, but rather evanescent odour), 6-phenylhexyl alcohol (b. p. 160 to 161° at 13 mm.; odour similar to that of the phenylamyl alcohol; not particularly pleasant) and 7-phenylheptyl alcohol, a liquid which boils between 170 and 172° (15 mm.) of a faint but particularly agreeable, rose-like aroma.

Aldehydes.

Isocitral. In our last Report (p. 145) we referred to *isogeraniol*, the alcohol which, according to Semmler and Schossberger, is generated when *enol-citral* acetate is reduced. *Isocitral*, the body corresponding with *isogeraniol*, has been described by Schossberger⁴⁾ in his inaugural thesis.

¹⁾ Proceed. chem. Soc. 28 (1912), 19

²⁾ Heintz, Liebigs Annalen 122 (1862), 269.

³⁾ J. v. Braun, Berl. Berichte 44 (1911), 2867.

⁴⁾ Zur Kenntnis des Carvenens und Terpinolens. Über *enol-Citralacetat*, *Isogeraniol* und *Isocitral*. Breslau 1911.

Isocitral is left as a residue when reduced enolised citral is treated with phthalic anhydride (for the purpose of isolating *isogeraniol*), and, when regenerated from the bisulphite-compound, forms a liquid with the following constants: b. p. 103 to 108° (15 mm.), $d_{20} 0,8976$, $n_D 1,4810$. It yields α -*isocitryl*- β -naphthocinchonic acid, m. p. 206° (from glacial acetic acid).

Benzaldehyde. For the purpose of preparing the labile benzaldehydephenylhydrazone discovered by Thiele and Pickard¹⁾, F. B. Thole²⁾ saturates a suspension of this hydrazone in concentrated hydrochloric acid with hydrogen chloride gas. The resulting red suspension is poured into excess of soda-solution, when the labile benzaldehydephenylhydrazone is precipitated in the form of a yellowish-white deposit. Recrystallised from glacial acetic acid, it melts at 136°, and when repeatedly recrystallised from this solvent it is gradually transformed into the stable modification, m. p. 152°.

Fatty-aromatic Aldehydes. J. v. Braun and O. Kruber³⁾ state that in the fatty-aromatic aldehydes, as in the fatty-aromatic alcohols, the odour gradually diminishes in intensity as the polymethylene chain lengthens⁴⁾. The authors prepared synthetically a series of fatty-aromatic aldehydes and found that with the majority the methods which have been worked out for preparing these bodies were failures, or yielded poor results. They obtained satisfactory yields, however, by reducing primary nitro compounds into aldoximes by Konowaloff's method⁵⁾, and recovering the aldehydes from the latter by saponification. Thus, for example, for the purpose of preparing the hydrocinnamic aldehyde, γ -iodopropylbenzene and silver nitrite were allowed to react, the result being γ -phenyl-propylnitrite and a satisfactory yield of phenylnitropropane. The sodium compound of phenylnitropropane in aqueous solution having been reduced with stannous chloride of tin and hydrochloric acid, the reaction-mixture was neutralised with soda and the resulting hydrocinnamic aldoxime extracted with ether. The best method of isolating the aldehyde is to heat at once with dilute sulphuric acid the residue which remains behind when the ether has been distilled off, after which the aldehyde may be distilled off with steam. Hydrocinnamic aldehyde yields a characteristic diphenylmethane dimethyldihydrazone, m. p. 99 to 100°. Working by the same method the authors obtained the following aldehydes: δ -phenylbutyric aldehyde (b. p. 129 to 131° at 7 mm.; odour fainter than that of hydrocinnamic aldehyde), δ -phenyl-*n*-valeraldehyde (b. p. 129 to 131° at 10 mm.; odour

¹⁾ Berl. Berichte **31** (1898), 1250.

²⁾ Proceed. chem. Soc. **27** (1911), 278.

³⁾ Berl. Berichte **45** (1912), 384.

⁴⁾ Comp. p. 181.

⁵⁾ Chem. Zentralbl. **1899**, I. 597, 1074.

resembling that of citral), α -phenylcapronic aldehyde (b. p. 141 to 144° at 9 mm.; faint odour), β -phenylcinnanthol (b. p. 155 to 159° at 9 mm.; m. p. of the nitrophenylhydrazone 68 to 70°).

Ketones.

W. L. Ipatiew, in collaboration with G. Balatschinsky¹⁾ has continued his experiments on catalytic reactions at high temperature²⁾ and high pressure, and has investigated the course of hydrogenation of unsaturated terpene ketones. The authors reduced *l*-carvone, *d*-pulegone and *d*-menthone with nickel oxide as a catalyser and hydrogen under high pressure at 220 to 280°, and found that hydrogenation is accomplished between 220 and 240°, no matter whether the double bond is in the ring or in the side-chain. The carbonyl-group is attacked between 260 and 280°, but in the case of the menthol series a temperature of 260° must not be exceeded, as otherwise menthane would be formed. The lower the temperature of the reaction, the less is the change in optical rotation. At 280° the reduction of carvone gives rise to carvomenthol, at 240° the double bond is attacked, while the keto-group remains unchanged. At 280° the hydrogenation of pulegone yields menthane, between 220 and 240°, menthone is formed. Menthone at 250° yielded a menthol, m. p. — 8° ($d_{20} = 0.8948$), which showed some similarity to the menthol obtained by Kondakow and Bachtshiew³⁾ in the reduction of diosphenol. It also resembles the menthol (m. p. — 9°) which was obtained in the hydrogenation of thymol at 260°.

Pinolone. The ketone pinolone⁴⁾, a conversion-product of pinol, has been found by Wallach⁵⁾ to be an acetyl*isopropylcyclopentane*. Wallach reduced the pinolone recovered from the semicarbazone by Paal's method, whereby he obtained a ketone $C_{15}H_{24}O$ (dihydropinolone, 1-acetyl-3-*isopropylcyclopentane*), possessing the following properties: b. p. 211°, $d_{20} = 0.8880$ to 0.8885, $n_{D21} = 1.4466$ to 1.4476. In contradistinction to pinolone, which has a yellow colour, dihydropinolone is colourless; a point of difference which is often found in saturated and in unsaturated ketones⁶⁾. Dihydropinolone semicarbazone melts at 164 to 165°. When dihydropinolone is oxidised with hypobromite liquor there results an acid (1,3-*isopropylcyclopentane* carboxylic acid), of which the amide, m. p. 164 to 165°, was identical with the body which was obtained by Semmler from camphenilone, and to

¹⁾ Berl. Bericht 44 (1911), 3461.

²⁾ Comp. Report April 1911, 166.

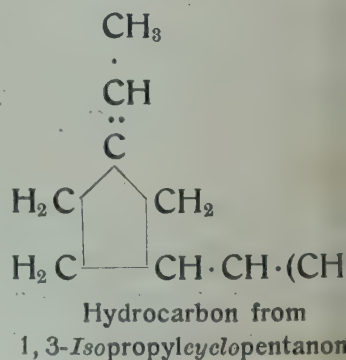
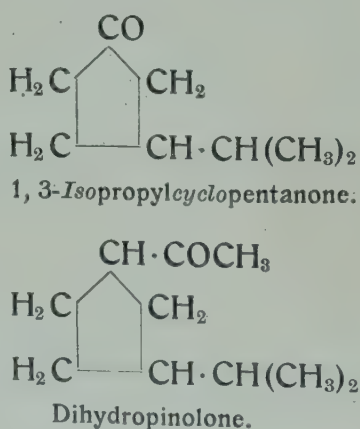
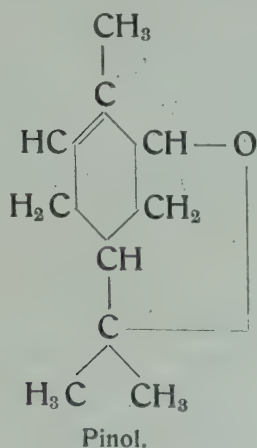
³⁾ Journ. f. prakt. Chem. II. 63 (1901), 61; Report April 1901, 71.

⁴⁾ Comp. Schimmel's Bericht, October 1899, 64.

⁵⁾ Liebigs Annalen 384 (1911), 193.

⁶⁾ Wallach, Terpene und Campher. Leipzig 1909, p. 169.

which he gave the name of dihydrocamphoceënic acid amide¹⁾. Bouveault and Blanc²⁾ have demonstrated that this compound is derived from 1,3-isopropylpentane carboxylic acid. By treating it with bromine and potash liquor this amide was converted by Wallach into the corresponding base, which contains one carbon atom less. This base was converted into the alcohol by treating it with nitrous acid, and the alcohol was oxidised with chromic acid, the result being the ketone 1,3-isopropylcyclopentanone. (m. p. of the semicarbazone 192 to 193°.) Dihydropinolone was prepared synthetically from 1,3-isopropylcyclopentanone by treating it with bromopropionic ester. The acid which is generated as the product of the reaction, when submitted to dry distillation, yielded a hydrocarbon, the nitrosochloride of which gave rise to a ketone which was reduced to dihydropinolone by Paal's method. This hydrocarbon, of which the formula probably corresponds in the main with that set forth below, was also prepared synthetically from dihydropinolone. Reduction of this ketone yielded dihydropinolol (b. p. 205 to 216°; d_{190} 0,8920; n_{D180} 1,4569) which, when warmed with chloride of zinc, gave rise to the hydrocarbon which was the object of the experiment (b. p. 171 to 174°; d_{220} 0,812; n_{D220} 1,4515).



According to a communication by W. Bonsdorff³⁾ the calcium salt of pinic acid, when subjected to dry distillation, does not yield the bicyclic ketone which would be expected, but most probably 1-isopropylene-2-ketopentamethylene. Bonsdorff obtained three fractions, which boiled at 4 mm. between 34 to 50°, 50 to 100° and 100 to 102°. These fractions do not react with semicarbazide-, thio-semicarbazide- or hydroxylamine hydrochloride, but fraction II, when treated with *free* semicarbazide yielded a semicarbazone, m. p. 159 to 161°, from which the ketone was regenerated. This ketone boiled between 69 and 71° (8 mm.), its other constants being as follows:

¹⁾ Comp. Report October 1906, 138.

²⁾ Comp. Report April 1908, 191.

³⁾ Berl. Berichte 44 (1911), 3208.

d_{40}^{20} 0,9355, n_{D20} 1,46660, mol. refr. 36,788. As stated above it is probably identical with 1-*isopropylene*-2-ketopentamethylene, for which the mol. refr. calculated was 36,488.

Santenone. According to Rimini¹⁾, the action of nitrous acid upon santenone oxime gives rise to a body possessing all the properties of a pernitroso-derivative; with hydroxylamine and with semicarbazide nitrous oxide is given off, with formation of santenone oxime or semicarbazone. If the body is treated with cold concentrated sulphuric acid, nitrous oxide is also given off, and an unsaturated compound results which yields a semicarbazone, m. p. 180°. The saturated santenone, when subjected to the same treatment, remains unchanged, and also yields a semicarbazone with m. p. 224°; hence the reaction first described had given rise to an isomeride, to which Rimini has given the name of *isosantenone*. The oxidation- and reduction-products of the new body which have been obtained up to the present hardly bear out the accuracy of Semmler's²⁾ santenone-formula.

It is expected that Rimini will shortly publish a more detailed paper showing how the process of conversion into an unsaturated body takes place; possibly, as in the case of camphor, there is a rupture of the bridge-formation and an "erection" of the bridge itself.

Menthone. In view of the circumstance that the reduction of menthone in alcoholic solution gives a poor yield, V. Skworzow³⁾ has reduced this ketone by Sabatier and Senderens' method, but also without obtaining favourable results. Ultimately, however, the following method was found to be effective: the ketone [consisting, in the case under review, of *l*-menthone ($[\alpha]_D - 14^\circ$) from buchu oil] is dissolved in a brass autoclave in ten times its volume of methyl or ethyl alcohol and treated with more than double the calculated quantity of sodium, in the course of which manipulation the liquid acquires a temperature of between 70 and 80°. The closed autoclave is shaken until the contents have cooled down completely and the reaction-product is then distilled off with steam. The result is a quantitative yield of a mixture of solid ($[\alpha]_D + 37,87^\circ$) and liquid ($\alpha_D + 16^\circ$) menthol. By the same method the reduction of pulegone (b. p. 222 to 223°; d_{180}^{40} 0,938; $\alpha_D + 24^\circ$) gives an almost quantitative yield of a mixture of solid and liquid *l*-menthol (b. p. 200 to 218°; $\alpha_D - 12^\circ$).

When applied to the reduction of dipentene, pinene, camphene, terpineol, and thymol, the method failed to yield positive results.

On the reduction of menthone, see also p. 183.

¹⁾ Rendiconti della Soc. chim. ital., Ser. 2, Vol. 4, Part 1, p. 2 (12 January 1912).

²⁾ Comp. Report October 1910, 120.

³⁾ Journ. f. prakt. Chem. II. 84 (1911), 422.

Some years ago we described Bœdtker's¹⁾ experiments in the action of Grignard's salts upon ethyl- and benzal-menthone, and in our notice we referred among other bodies to menthodiphenylmethane, which occurs in the form of three isomerides. Bœdtker²⁾ has now oxidised with chromic acid in a glacial acetic acid solution the modifications of menthodiphenylmethane which melt at 140° and between 136 and 137° respectively, and has obtained benzophenone, which proves that the two phenyl groups are found at the same carbon atom.

Bœdtker prepared menthomethylphenylmethane by condensing benzylidenementhone with magnesiummethyl iodide: m. p. 111 to 112° ; $[\alpha]_{D19} + 95^{\circ} 16'$ (in benzene), of which the benzoate melts at 152 to 153° . He also describes menthylisoamyl phenylmethane: b. p. 215° (15 mm.), $[\alpha]_{D20,50} + 13^{\circ} 45'$ (in benzene solution), which yields a benzoate melting between 93 and 94° .

In conclusion Bœdtker mentions benzoylmenthone, a liquid with b. p. 185° (12 mm.) ($[\alpha]_{D20,50} + 30^{\circ} 11'$ in benzene solution, $n_{D21,80} 1,51745$).

By condensing natural menthone (b. p. 208 to 209° ; $d_{00} 0,8941$; $[\alpha]_D - 23,6^{\circ}$) with magnesium phenyl bromide, M. Murat³⁾ has prepared the tertiary alcohol methyl-1-phenyl-3-isopropyl-4-cyclohexanol-3: b. p. 175° (20 mm.), $d_{00} 0,9962$, $d_{200} 0,9843$, $n_D 1,527$. No phenylurethane was obtained. Treatment of the alcohol with water-eliminating agents (the readiest method being by passing it over aluminium at 300°) gives rise to methyl-1-phenyl-3-isopropyl-4-cyclohexene (b. p. 268 to 272° ; $d_{00} 0,9700$; $d_{200} 0,9621$; $n_D 1,537$).

When treated with magnesium cyclohexyl chloride menthone yields methyl-1-cyclohexyl-3-isopropyl-4-cyclohexanol-3 (cyclohexylmenthol) (m. p. 92°), from which, by splitting off water, methyl-1-cyclohexyl-3-isopropyl-4-cyclohexene, results. This hydrocarbon has an odour of garlic and possesses the following constants: b. p. 265° , $[\alpha]_D + 6,2^{\circ}$, $d_{00} 0,9897$, $d_{140} 0,9198$, $n_D 1,498$.

Murat has also carried out the reaction of thymomenthone with magnesium phenyl bromide. This ketone, which has b. p. 212° , he prepared by passing thymomenthol over copper heated to 300° . *i*-Phenylthymomenthol possesses the following constants: b. p. 170° (18 mm.), $d_{00} 0,9950$, $n_{D180} 1,526$. The corresponding menthene boils between 270 and 272° .

The boiling point of *i*-cyclohexylthymomenthol, a body which results from the condensation of thymomenthone with cyclohexyl magnesium bromide, is about 164° (15 mm., with partial decomposition): $d_{00} 0,9931$, $n_{170} 1,529$. This body yields a cyclohexylthymomenthene with b. p. 260° (756 mm.).

¹⁾ Compt. rend. **145** (1907), 392; Report October 1907, 160.

²⁾ Compt. rend. **154** (1912), 437.

³⁾ Journ. de Pharm. et Chim. **108** (1911), 294.

Camphor. As a result of their investigations, G. L. Blanc and J. F. Thorpe¹⁾ have found that when methyl-diketo camphoric acid is reduced by Komppa's method, the methyl-group remains in combination with carbon; from which it follows that their criticism of Komppa's camphoric acid synthesis is without foundation²⁾.

Isocamphenilone. If, as is generally assumed to be the case, camphenilone and fenchone are homologues, it would follow (as we gather from a paper by Komppa)³⁾, that the hydrating of camphenilene (a hydrocarbon which corresponds to camphenilone) would give rise to a new alcohol, differing from camphenilol, and that oxidation of this alcohol would yield a new ketone: *isocamphenilone*, analogous to the preparation of *isofenchyl* alcohol from fenchene by Bertram and Helle. As a matter of fact, Komppa, by hydrating camphenilene, obtained a new secondary alcohol $C_9H_{15}OH$, *isocamphenilol* (b. p. 196° at 740 mm.), which he oxidised into *isocamphenilone*, a ketone with a camphoraceous odour. The best method of obtaining camphenilene is by heating camphenyl chloride with aniline. It possesses the following constants: b. p. 140° (755 mm.), $d_{20} 0,8693$.

Isofenchone. A good many years ago Bertram and Helle, working in our laboratory⁴⁾ upon *D-l*-fenchene, had prepared therefrom the *i-iso*-fenchyl alcohol and from the latter, by oxidation, the ketone $C_{10}H_{16}O$, which was subsequently designated *isofenchone* by Wallach⁵⁾. The last-named investigator, when oxidising *isofenchone* with permanganate of potassium in alcoholic solution, obtained *l-isofenchocamphoric* acid, in which respect *isofenchone* is sharply differentiated from fenchone⁶⁾. Aschan⁷⁾ has determined the constitution of this acid as follows: 1. The dibasic acid is saturated; both v. Bæyer's permanganate test and the bromine-absorption test give negative results; ester-refraction normal. 2. The acid shows a pronounced tendency towards the formation of anhydride. This symptom, together with the fact that when the calcium salt is distilled it does not afford a simple cyclic ketone, indicate a cyclically substituted *cis*-glutaric or succinic acid. 3. The fact that the acid, when heated with a mixture of glacial acetic and hydrochloric acids, is partially convertible into a geometrically isomeric form, viz., *trans-isofenchocamphoric* acid (m. p. 169 to $170,5^\circ$), shows that the carboxyl which plays a part in the conversion-process is linked directly with the carbon. 4. The *cis*-acid,

¹⁾ Journ. chem. Soc. 99 (1911), 2010; Bull. Soc. chim. IV. 9 (1911), 1068.

²⁾ Comp. Report October 1909, 198; April 1910, 178; October 1910, 196; April 1911, 182; October 1911, 147.

³⁾ Liebigs Annalen 387 (1912), 293.

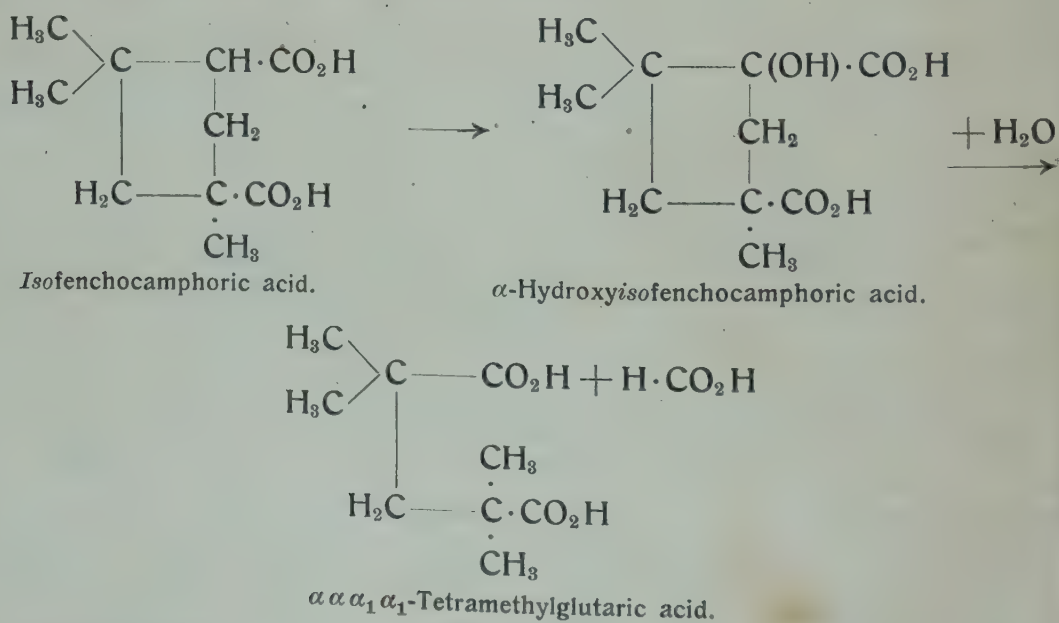
⁴⁾ Journ. f. prakt. Chem. II. 61 (1900), 293; Report April 1900, 56.

⁵⁾ Comp. Report April 1908, 179.

⁶⁾ Comp. Report April 1908, 179; November 1908, 190.

⁷⁾ Liebig's Annalen 387 (1912), 1.

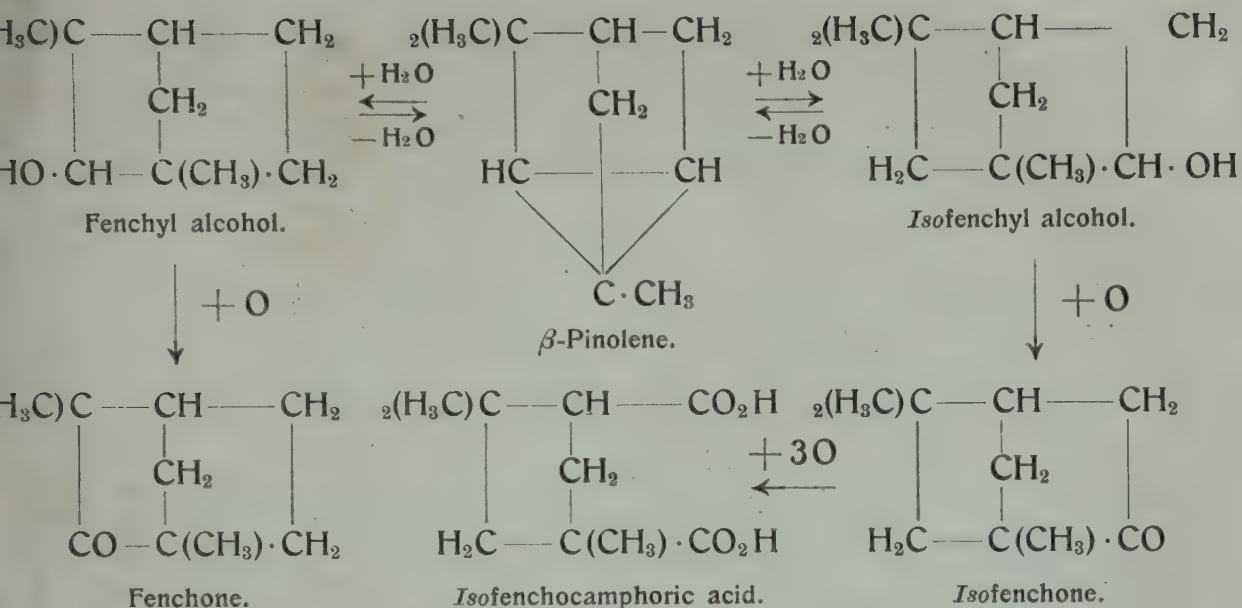
or its chloride, can be readily brominated, giving rise to two geometrically isomeric α -bromo-*isofenchocamphoric* acids. But only one bromine atom reacts readily, from which follows that the second carboxyl is linked with the quaternary carbon-atom. 5. The action of bases upon the high-boiling α -brominated acid gives rise to dehydro*isofenchocamphoric* acid, indicating that in *isofenchocamphoric* acid the group $\text{C} \begin{array}{c} \text{---} \text{CH} \text{---} \text{CO}_2\text{H} \\ | \\ \text{CH} \\ | \end{array}$ is present. 6. The formation of a stable lactone acid (*iso-fenchocamphanic* acid) from α -hydroxy-*isofenchocamphoric* acid points to the second carboxyl occupying the γ -position towards the hydroxyl of the hydroxy-acid. This hydroxyl is linked to the same cyclic-carbon as is the first-named; hence *isofenchocamphoric* acid is a cyclically-substituted glutaric acid. 7. Careful melting of *isofenchocamphoric* acid with potash gives rise to formic acid and to $\alpha\alpha\alpha_1\alpha_1$ -tetramethyl glutaric acid. 8. In the course of the operation of melting with potash there is formed, in addition to tetramethyl glutaric acid, a keto-acid, which when subjected to further melting, is converted into tetramethyl-glutaric acid. According to Aschan the conversion of the α -hydroxy-acid during the melting with potash takes place as follows: —



β -Pinolene¹⁾, when heated with glacial acetic and sulphuric acid yields *isofenchyl* alcohol; and is therefore closely allied to this body, as well as to *isofenchone*. In addition to *isofenchyl* alcohol, the β -pinolene (or *cyclofenchene*, to give it the name proposed by Aschan for the future), yields *isofenchyl* alcohol. The reaction is graphically explained below. The formula for *isofenchone* assumed by Aschan on the basis of the experimental material collected by him is the same as that which was drawn up by Semmler²⁾ without any experimental warrant.

¹⁾ Comp. Report October 1909, 169.

²⁾ Semmler, *Die ätherischen Öle*, Vol. III, p. 569.



It would lead us too far to give an explanation of the formation of the fenchene compounds from pinene and of the author's theory of the formation of geometric isomerides in the bromination of dibasic alicyclic acids with hydrogen in the α -position, and in the re-substitution of the α -bromoderivatives. Nor are we able to enter into further details of the rich experimental material.

On the reduction of pulegone, see p. 183.

Carvone. When molecular quantities of hydrogen cyanide and carvone are allowed to react at ordinary temperature, the resulting product is cyanodihydrocarvone¹⁾, m. p. 93,5 to 94,5°; ($[\alpha]_D + 13,5^\circ$). When the reaction is carried out in hot alcoholic solution the result, according to A. Lapworth and V. Steele²⁾, is an isomeric product, β -cyanodihydrocarvone, m. p. 84° ($[\alpha]_D - 42,1^\circ$). In the presence of bases this body shows the effect of mutarotation.

When a mixture of carvone hydrosulphide and aqueous solution of potassium cyanide is diluted with glacial acetic acid, the result, as shown by V. Steele³⁾, is the generation of a dinitrile, with elimination of water. The dinitrile has the following formula p. 190.

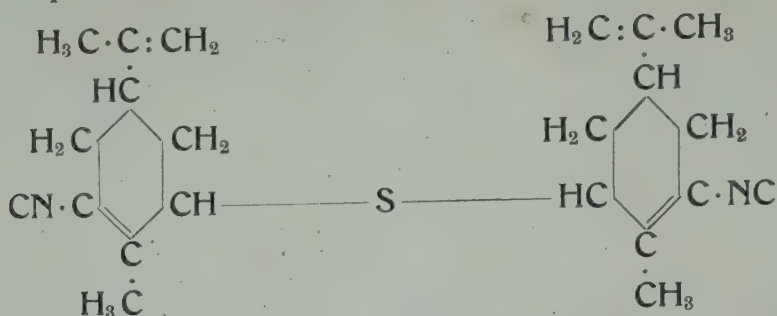
It melts at 94°, and has opt. rot. $[\alpha]_{D_{120}} + 4,02^\circ$ (0,4062 g. substance to 25 cc. alcohol). When heated with ferrous hydroxide and alkali it readily loses both its hydrogen sulphide and hydrogen cyanide. When heated with concentrated aqueous hydrobromic acid solution, the nitrile is partly

¹⁾ Comp. Report October 1906, 132.

²⁾ Journ. chem. Soc. 99 (1911), 1877.

³⁾ Proceed. chem. Soc. 27 (1911), 240.

hydrolysed, giving rise to a dibasic acid $(C_{10}H_{14} \cdot CO_2H)_2S$, contaminated with a neutral product.



In previous Reports (October 1906, 130, 131; November 1908, 186) we have discussed the investigations of Rupe and Liechtenhan, of Klages and Sommer, and of Rupe and Emmerich into the hydrocarbon methylmenthatriene, which is generated by treating carvone with magnesium methyl iodide. Rupe and Kerkovius¹⁾ have further pursued these investigations and have prepared a hydrocarbon of greater stability than methyl menthatriene, namely tetramethyl *cycloheptatriene*, which is readily obtainable from eucarvone and magnesium methyl iodide. The first product is a tertiary alcohol which gives off water at water-bath temperature and is converted into the hydrocarbon. The latter forms a very mobile liquid, with an odour reminding first of camphor and then of cajuput oil: b. p. 67 to 68° (11 mm.), $d_{20} 0.8687$, $n_{D20} 1.50660$. When reduced with alcohol and sodium it yields tetramethyl *cycloheptadiene*.

A modification of the process by allowing eucarvone and methyl iodide to flow on to the magnesium, yields, in addition to the hydrocarbon, two solid bodies, m. p. respectively 177 to 178° and 142 to 143°. These bodies are probably stereomeric and represent dimolecular methyl derivatives of dihydroeucarvone.

Phenols.

Dicarvacrol. On p. 200 of our Report of October 1910 we referred to dehydrodicarvacrol (dicarvacrol), a body which has been obtained by Cousin and Hérissé by acting with ferric chloride upon an aqueous carvacrol solution. Since then, Cousin²⁾ has investigated the action of bromine and chlorine upon dehydrodicarvacrol and has described a few well-defined halogen-compounds.

Oxides.

Cineole. G. Cohn³⁾ has established that cineole combines with 1,5 dihydroxy-naphthalene to form a double-compound which crystallises in the

¹⁾ Berl. Berichte 44 (1911), 2702.

²⁾ Compt. rend. 154 (1912), 441.

³⁾ Pharm. Zentralh. 53 (1912), 32.

form of beautiful yellow needles, and which may be readily split up into its constituents by alkalies. He has also observed that coumaric acid readily reacts with cineole under heat, forming a double compound from which cineole can be immediately regenerated by treatment with soda liquor.

Acids.

Camphocarboxylic acid. Camphocarboxylic acid, which is not reducible by the usual methods, may, as discovered by Bredt in collaboration with Burkheiser and Sandkuhl¹⁾, be reduced to borneol carboxylic acid by the electrolytic method. According to Bredt²⁾, camphononic acid behaves similarly, being electrically reducible to camphonolic acid (dihydrocamphononic acid). The camphononic acid was prepared by the modified Lapworth-and-Lenton method, by preparing free hydroxycamphoraminic acid from camphanic acid amide, and submitting the sodium salt of this acid to Hofmann's reaction with exactly determined quantities of bromine and alkali. The actual yield averaged from 67 to 69% of the theoretical. 10 grams camphononic acid electrically reduced yielded 9 grams reduction-product, containing 4.5 grams camphonololactone, the remainder consisting of *cis-trans*-camphonolic acid and of unattacked camphononic acid. The camphonololactone boils at 239.2° and melts between 160 and 161°. Boiling of the lactone with aqueous baryta solution afforded *cis*-camphonolate of barium, from which the free hydroxy acid was separated with hydrochloric acid by cooling in ice. This body has no true melting-point, being partly converted, when heated, into the lactone, owing to elimination of water. The *cis-trans*-camphonolic acid which was isolated from the reduction-mixture by extraction with soda solution formed bunches of crystals, m. p. 249 to 250°.

Camphononic acid can be reduced with sodium amalgam without the aid of the electric current, but in this case the reaction is exceedingly slow. With 30 grams acid it required over 50 hours, the amalgam having to be renewed no fewer than seven times, 1000 grams being taken up each time. When the camphonololactone is shaken with saturated hydrobromic acid, γ -bromo camphononic acid (m. p. 146 to 147°) is formed. When the camphonololactone and the *cis-trans*-camphonolic acid are oxidised with nitric acid camphoronic acid is generated.

Bornylene carboxylic acid. A few years ago, Bredt and Sandkuhl³⁾ had made the remarkable discovery that hydrobromic acid reacts with bornylene carboxylic acid, giving rise to various bodies according to whether the reaction is carried out in an aqueous or in an anhydrous

¹⁾ Comp. Report October 1906, 135; Report October 1909, 192.

²⁾ Journ. f. prakt. Chem. II. 84 (1911), 786.

³⁾ Liebigs Annalen 366 (1909), 39; Report October 1909, 194.

solution. In the latter case the reaction usually takes a normal course. Basing themselves upon the results thus obtained, Bredt and Sandkuhl¹⁾, for the purpose of preparing the β -hydriodo-bornylene carboxylic acid solution, saturated the bornylene carboxylic acid in a solution of glacial acetic acid with hydriodic acid. The free β -hydriodo-bornylene carboxylic acid occurs in beautiful needle-shaped crystals, m. p. 129 to 130°. Its sodium salt, in analogy with β -hydrobromo-bornylene carboxylic acid, yields, when boiled with soda-liquor, bornylene carboxylic acid together with small proportions of bornylene (m. p. 113°; b. p. 146° at 745,5 mm.; $[\alpha]_{D20} - 23,68^\circ$ in toluene solution). When heated with glacial acetic acid + sulphuric acid, bornylene yields a body with an odour reminding of *isobornyl* acetate, b. p. 103 to 104° (14 mm.) which upon saponification afforded a borneol with a not very sharp m. p.

Bornylene carboxylic acid yields a dibromo-derivative, m. p. 159 to 160°. When β -hydriodo-bornylene carboxylic acid is reduced it yields hydro-bornylene carboxylic acid (b. p. 171° at 22 mm.). The chloride boils between 114 and 115° (14 mm.), and the amide has m. p. 166 to 167°.

Cinnamic Acid. Several detailed investigations into the conditions of isomerism in cinnamic acid have again been published, and to these we will briefly refer in connection with our previous notes²⁾. E. Erlenmeyer³⁾ in his paper on labile interconvertible isomerides of similar structure, discusses the conditions of isomerism which have been observed in the various cinnamic acids. Investigation of the labile cinnamic acids of the *iso*-series showed that here we have to deal with cases of isomerism which cannot be explained either by the atomic structure or stereo-chemically, and of which the differences must be assigned to a still unknown difference in the position of some parts or other of the molecules. Although the lability of the acids is not so great as to cause the differences in the modifications to disappear in the melting, it would yet seem that certain conditions exist in which the lability is very considerable, and this explains why Stobbe⁴⁾ (see p. 195) in one case obtained from the three acids solutions in which by his experimental method he was unable to detect any differences. The conditions referred to above, however, cannot as yet be experimentally determined. In forming a judgment of the conditions of isomerism which exist in this case the fact is of great importance that the *allo*-acid, by being brought under the influence of heat, is finally converted into the most labile of all acids, — the *iso*-acid of Erlenmeyer sen. The

¹⁾ Journ. f. prakt. Chem. II. 84 (1911), 778.

²⁾ Comp. Report April 1907, 155; April 1909, 138, October 1909, 210; April 1910, 188; October 1910, 203.

³⁾ Biochem. Zeitschr. 34 (1911), 306. Copies of this and the other reprints here referred to were kindly sent to us by the authors.

⁴⁾ Berl. Berichte 43 (1911), 506.

last-named acid must be regarded as being the most labile and the richest in energy, and the *allo*-acid as the most stable and the most deficient in energy. Between the two stands Liebermann's *iso*-acid.

A second paper by Erlenmeyer¹⁾ deals with the isomeric acids of the cinnamic acid series. It has been demonstrated by various methods that synthetic cinnamic acid is a uniform crystallising mixture of storacic and hetero-cinnamic acids. But, as we have already mentioned in previous references to the matter, the objection has been raised that the difference between hetero- and storacic-cinnamic acid may have been caused by some impurity in the hetero-cinnamic acid. It is scarcely possible, in certain circumstances, to invalidate this objection, especially if it be assumed that the impurity is so small as to be no longer detectable by the available methods. In order to disprove this hypothesis of contamination, Erlenmeyer has made a symposium of the differences which have been found to exist in the past and recently between storacic and synthetic cinnamic acids on the one hand and storacic and hetero-cinnamic acids on the other. He has next described two methods by which it is possible to give convincing proof of the structural identity of storacic and hetero-cinnamic acids.

In common with cinnamic acid, benzaldehyde also appears to occur in several modifications. From the detailed communications by Erlenmeyer, G. Hilgendorff and T. Marx²⁾ on separation and conversion in the benzaldehydes we abstract the following particulars: In Perkin's reaction the natural benzaldehyde, before being deprived of its hydrocyanic acid, gives rise to storacic-cinnamic acid, and after the elimination of hydrocyanic acid, to synthetic, and in some cases to hetero-cinnamic acid. The behaviour of the natural benzaldehyde before and after being deprived of its hydrocyanic acid is very different, not only under condensation but also under distillation. It would appear that natural benzaldehyde before the abstraction of its hydrocyanic acid consists principally of storacic benzaldehyde, whereas benzaldehyde deprived of its hydrocyanic acid is composed of a mixture of storacic and hetero-benzaldehydes, from which under condensation synthetic cinnamic acid is generated. But it is not possible to base upon the distillation a method of separating the various benzaldehydes. The conditions are more favourable when the separation, which is based upon the varying rates of velocity of the reaction, is taken as the basis, but this method has the disadvantage that only one of the two components can be recovered, as the other undergoes a change in the course of the reaction. Erlenmeyer looks for the causes of the differences in the cinnamic acids and benzaldehydes in the benzene-nucleus itself, and it is to be assumed with v. Baeyer that it is possible for the benzene

¹⁾ Biochem. Zeitschr. **34** (1911), 355.

²⁾ Biochem. Zeitschr. **34** (1911), 386.

nucleus to exist under conditions of different stability which are susceptible of inter-conversion.

According to Erlenmeyer the esters of cinnamic acid and the benzaldehydes may be differentiated by their odour by those who have acquired some experience in this field of investigation. Of the two benzaldehydes for instance, hetero-benzaldehyde has a much more acrid odour than storacic benzaldehyde, of which the odour is bland.

The detection of the differences in the properties of the cinnamic acids and benzaldehydes to which reference is made above has induced the authors to extend their research to the investigation of benzene and styrene, and here they discovered similar differences as in the benzaldehydes. Other differences, such as the formation of various derivatives and differences in the rates of velocity of reaction cannot, according to Erlenmeyer, be expected in isomerides of identical atomic structure. These isomerides, however, must be distinguished by differences in energy.

In order to discover whether the peculiar behaviour of the cinnamic acids may perhaps be due to impurities arising from derivatives, Erlenmeyer and Hilgendorff¹⁾ have prepared mixtures of storacic cinnamic acid with various such derivatives. They examined mixtures with *p*-, *o*-, and *m*-chlorocinnamic acid, with *p*-, *m*-, and *o*-hydroxycinnamic acid, with *o*- and *p*-methoxycinnamic acid and with methylcinnamic acids. Among all the mixtures which were prepared by the authors that consisting of 1 part *p*-methoxycinnamic acid and 99 parts storacic cinnamic acid resembles synthetic cinnamic acid to a quite extraordinary degree, but the presence of the acid may be proved beyond doubt by oxidation and separation of the terephthalic acid. Attempts at oxidation with heterocinnamic acid afforded no trace of terephthalic acid. When a mixture contains 10% methylcinnamic acid that body may be removed by fractional precipitation, but a 20% content of methylcinnamic acid cannot be detected by combustion. The result of the crystallographic examination of the various mixtures was that of all the admixtures recorded above only that with methylcinnamic acid makes a mixture with any resemblance to synthetic cinnamic acid.

So far it had not been established whether the two constituent storacic and hetero-cinnamic acids, which have been separated out from synthetic cinnamic acid could be further split up. The results of investigations into this subject which have been carried out by Erlenmeyer and G. Hilgendorff²⁾ agree that synthetic cinnamic acid prepared from chloroform free benzaldehyde or from natural bitter almond oil free from hydrocyanic acid, does not owe such of its properties as differ from those of storacic cinnamic acid to any impurity, but that it consists of a mixture of storacic cinnamic acid and hetero-cinnamic acid which crystallise together.

¹⁾ Biochem. Zeitschr. 34 (1912), 405.

²⁾ Biochem. Zeitschr. 34 (1912), 417.

In conclusion, Erlenmeyer and Hilgendorff¹⁾, and Erlenmeyer²⁾, in connection with the investigations mentioned above, engage in theoretical considerations of the problem whether molecular asymmetric storacic cinnamic acids can exist, and of isomerism in ethylene derivatives. We regret that considerations of space compel us to restrict ourselves to a bare mention of these interesting questions.

The chlorine-free benzaldehyde, and part of the natural bitter almond oil used in these investigations had been placed at the authors' disposal by us.

Some further reference must also be made to the researches of H. Stobbe and F. Reuss³⁾, and of Stobbe⁴⁾. Stobbe and Reuss investigated the optical refraction of the melted acids and discovered that in a range of temperature of about 50° the meltings of *allo*- and *isocinnamic* acids have the same refraction and that therefore they must be regarded as optically identical. Stobbe (*loc. cit.*) has further occupied himself with the conversions of the *allo*- and *isocinnamic* acids in the flux and in the crystalline form. His conclusion is that there exist two different isomeric cinnamic acids, *viz.*, monomorphous *allocinnamic* acid (m. p. 68°) and dimorphous *isocinnamic* acid (m. p. 58° and 42°). This so-called-conclusion appears to him to afford the best summary of the *allo*- and *isocinnamic* acid question, taking also into account the results obtained by all other investigators.

According to Meyer⁵⁾, the researches of Stobbe do not supply sufficient experimental material to warrant the adoption of the theory of chemical isomerism between the *allocinnamic* acid with m. p. 68° on the one hand and the acids melting at 58 and 42° on the other.

Finally, H. R. Kruyt⁶⁾ controverts not only Stobbe but also Meyer's criticism of the latter.

Nitrogenous bodies.

According to N. Kishner⁷⁾ hydrazine compounds are capable of being resolved into hydrocarbons and nitrogen by boiling them with solid potassium hydroxide. Thus, 1,3-methylcyclohexylidene hydrazine yields methylcyclohexane; camphylidene hydrazine (m. p. 53 to 55°) yields camphane (m. p. 158 to 159°); fenchylidene hydrazine yields fenchane (b. p. 151,5°) and cyclohexylidene hydrazine hydrate yields cyclohexane. The dihydro-

¹⁾ Biochem. Zeitschr. 35 (1912), 134.

²⁾ *Ibidem* 149.

³⁾ Berl. Berichte 44 (1911), 2735.

⁴⁾ *Ibidem* 2739.

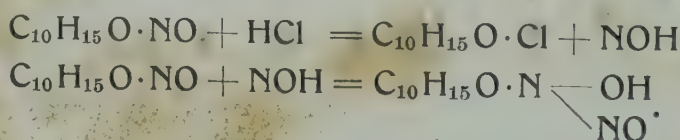
⁵⁾ *Ibidem* 2966.

⁶⁾ *Ibidem* 3108.

⁷⁾ Journ. russ. phys. chem. Ges. 43 (1911), 582, 951. Quoted from Chem. Zentralbl. 1911, II. 363, 1925.

carvone hydrazine compound affords $\Delta^{8,9}$ -menthene (b. p. 170°). With fuming hydrobromic acid, $\Delta^{8,9}$ -menthene yields a bromide which, upon being boiled with aniline, affords $\Delta^{4,8}$ -menthene (b. p. $170,5$ to $172,5^{\circ}$), and with 20% sulphuric acid, Δ^3 -menthene. The carvenone hydrazine compound, when heated with solid potassium hydroxide, yields Δ^3 -menther. The citronellal hydrazine compound yields a hydrocarbon $C_{10}H_{18}$, b. p. $164,5$. The hydrazine compound of citral gives rise to a hydrocarbon $C_{10}H_{18}$ (b. p. 164 to 165°).

v. Baeyer assumes that the relation of bisnitrosyl carone to carone bisnitrosylic acid, which is obtained by treating the first-named body with hydrochloric or sulphuric acid, corresponds to the relation of ether to alcohol. Bamberger¹⁾, however, takes another view of the conversion. He argues from the known fact that all the *C*-nitroso bodies are capable of forming monomolecular solutions, and that the bimolecular forms are less energetic than the monomolecular forms. The last-named he regards as the reactions of all *C*-nitroso compounds, including the bisnitrositised. In his opinion the conversion of bisnitrosylcarone yields first monomolecular nitrosyl carone, which latter is split up by the action of hydrogen chloride into chlorocarone and Angeli's nitroxyle. The latter, with a second molecule of nitrosocarone, affords carone bisnitrosylic acid (carone nitrosohydroxylamine, the conversion proceeding as follows: —



Bamberger's views are based upon observations made by him and v. Baeyer's own researches on the conversions: bisnitrosyl menthone $\rightarrow$ menthone-bisnitrosylic acid and chloromenthone, and bisnitroso pulegone $\rightarrow$ pulegone-bisnitrosylic acid and chloropulegone. The change in colour which is observed when a solution of *isosafrol*- or *anethol*-pseudonitrosite is alternately warmed and cooled down in glacial acetic acid, benzene or chloroform, is attributed by Bamberger to a manifestation of desmotropy, but he does not oppose the view that, in the main, a decomposition of a different kind takes place when the solutions are warmed.

Dihydrocarvylamine. According to G. F. Morrell²⁾, when an ethereal solution of dihydrocarvylamine is saturated with hydrochloric acid gas, the result is a chlorinated base, chlorotetrahydrocarvylamine (m. p. 205°), which, when heated with pyridine, yields a mixture of α - and β -dihydroterpenylamine. Both bodies are difficult to obtain in the pure

¹⁾ Berl. Berichte 44 (1911), 3066.

²⁾ Berl. Berichte 44 (1911), 2560.

ate. Benzoyl- α -dihydroterpenylamine has m. p. 219° , and when ozonised yields 2-benzoylamino-1-methylcyclohexanone-4 and acetone, which fact acidates the constitution of dihydroterpenylamine. Benzoyl- β -dihydroterpenylamine melts between 178° und 179° .

Benzoyldihydrocarvylamine, when treated with ozone, is converted into methyl-2-benzoylamino-4-ethanoylcyclohexane.

On the occurrence of indole in *Citrus*-flowers, see p. 165.

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